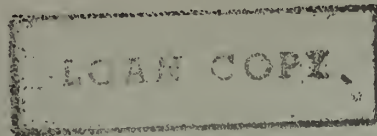
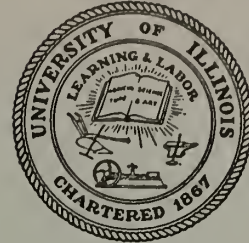


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# FILTRATION AS RELATED TO THE REMOVAL OF IRON FROM GROUND WATERS

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By

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University of Illinois, 1965

In evaluating the effectiveness of a number of iron removal plants in Illinois, it was observed that, in almost every plant investigated, a marked depletion of dissolved oxygen occurred in the filters. This observation was often associated with a high iron content in the filtered water, a large fraction of the iron being in the divalent form.

Consequently, a field study was initiated using a pilot iron removal plant at Clinton, Illinois, in an effort to determine the causes of the conditions leading to the passage of iron by the rapid sand filters. Studies were made to determine the effect of the biological growth in a filter on iron removal. In particular, the chemical changes mediated microbially and the effect of such changes on iron removal by filtration were investigated.

It was observed that during the first 8 to 10 weeks of operation using a new clean filter, iron removal was quite satisfactory. There was little biological growth in the filter and, consequently, there was no depletion of dissolved oxygen. In addition, there were no significant changes in the pH and  $E_h$  values of the water as it passed through the filter.

During operation of the pilot plant, it was not found possible to oxidize all of the soluble ferrous iron in the raw water even at a dissolved oxygen concentration of 7 mg/l. The incomplete oxidation of soluble ferrous iron was believed to be due to the precipitation of a portion of

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the iron as  $\text{FeCO}_3 \cdot \text{Fe}(\text{OH})_2$ . The formation of a ferrous complex,  $\text{FeHCO}_3^+$ , as well as the adsorption of ferrous iron on ferric hydrate floc were also postulated. A reaction-sedimentation time of 48 minutes provided in the pilot plant was found to be insufficient to settle insoluble iron in the reaction-sedimentation tank. This was apparently due to a stable ferric iron sol.

At the end of 8 to 10 weeks, the filter was ripened. Considerable biological growth was evident, the filter effluent was devoid of dissolved oxygen, and there was evidence that nitrification was taking place in the filter. The amount of oxygen depleted was proportional to the amount of ammonia oxidized. Under these conditions a reduction of iron from the ferric to the ferrous form occurred which was associated with a decrease in the observed  $E_h$  of the water. There was also a decrease in the pH of the filtered water with time accompanied by an increase in the amount of soluble ferrous iron passed by the filter.

Studies on the filtration of iron were made where thiourea, a known inhibitor for Nitrosomonas, and "Roccal," a general bacterial inhibitor, were added to the filter influent. Nitrification was stopped completely at a dosage of 7.6 mg/l ( $10^{-4}$  M) of thiourea. The overall bacterial growth was minimized at a dosage of 5 ml/l of 10 percent "Roccal" solution. With the addition of the inhibitors, there was no loss of dissolved oxygen and no reduction of ferric iron in the filter.

Studies on the effect of prechlorination were made using a ripened filter. Nitrification was stopped employing a chlorine dosage of 50 mg/l. A residual of 1 mg/l could be maintained in the effluent. The filter did not pass any ferrous iron under these conditions.



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## 1. INTRODUCTION

### 1.1 Nature of the Problem

One of the most common constituents of natural waters is iron. It occurs in both ground and surface waters. The significance of iron in ground waters may be illustrated by considering the public water supplies in the State of Illinois. Of the 971 total water supplies serving municipalities, 674 use ground water as a source of supply. Approximately 75 percent of these ground waters contain iron in excess of 0.3 mg/l (1). As a result, some 35 percent of these supplies are treated for iron removal. It has been reported that about one third of the treatment plants that practice iron removal in the State of Illinois fail to produce waters to meet the USPHS recommended limit with regard to iron.

According to the USPHS 1962 Drinking Water Standards, the recommended limit for iron in public water supplies is 0.3 mg/l (2). Because iron is essential for proper nutrition, this limit is not based on any physiological consideration. Iron is objectionable because of the staining of laundry and porcelain ware. On exposure to air, soluble ferrous iron is oxidized to the insoluble ferric state. This often results in the formation of a brown precipitate and a condition commonly referred to as "red water." Precipitated iron may also cause clogging problems in filters, in ion exchange softeners, and even in distribution systems. The presence of iron in water supplies may support the growth of iron bacteria, again leading to problems of clogging and customer complaints. Taste problems in water and other beverages have also been associated with the presence of iron (3). Thus, the recommended limit for iron in domestic water supplies

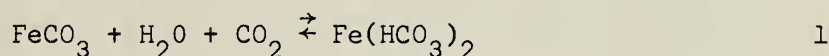


is based on aesthetic, taste, and nuisance considerations. Industry, on the other hand, may have more demanding requirements as to the critical concentration of iron in their process or cooling waters. This will vary with the industry.

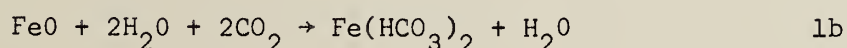
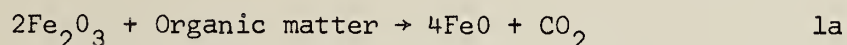
## 1.2 Mechanisms of Solution of Iron

For the most part, iron exists in natural ground waters in the soluble ferrous state. Just how iron dissolves in water in contact with soils containing insoluble ferric oxides or ferrous carbonate has not been entirely resolved. The mechanisms commonly cited by which iron may enter ground waters are:

a) solution due to the presence of excess carbon dioxide,  $\text{CO}_2$ , which converts insoluble ferrous carbonate,  $\text{FeCO}_3$ , into highly soluble ferrous bicarbonate,  $\text{Fe}(\text{HCO}_3)_2$ , as typified in Equation 1 below



b) solution under anaerobic conditions, possibly mediated by soil bacteria which reduce ferric iron to the ferrous form in the first step of the mechanism. Some reduced inorganic ( $\text{H}_2\text{S}$ ) and organic compounds may also perform this reduction under anaerobic conditions of ground waters. Equations 1a and 1b represent such a mechanism.



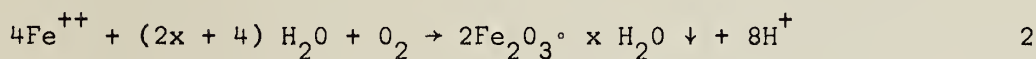


c) solution of the organic color bodies from vegetative growths in which iron (ferrous and ferric) is complexed with many stable organic compounds (4). Iron introduced by (a) and (b) of the above mechanisms of solution is mainly responsible for the presence of iron in ground water supplies.

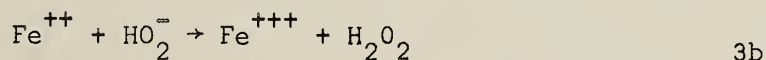
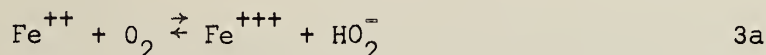
Because of the problems caused by the presence of iron in water supplies, the practice of iron removal was started as early as 1874 in Germany as reported by Weston (5).

### 1.3 Oxidative Processes for Iron Removal

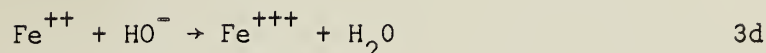
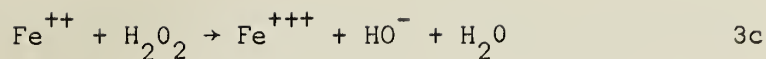
Oxidation processes are generally used to remove soluble iron from ground waters. In essence this is a reversal of the natural process whereby iron is rendered soluble. The most commonly used oxidizing agent is oxygen, which is added to the water by means of aeration. It has been accepted that the reaction leads to the formation of hydrated ferric oxides, according to the general overall equation which combines oxidation with hydrolysis:



Stoichiometrically, 1 mg/l of oxygen will oxidize 7 mg/l of ferrous iron. Weiss (6) reported that the oxidation of ferrous iron proceeds in a step-wise fashion as shown below:







These reactions are not balanced with respect to hydrogen ions and are not intended to specify the dependence of reaction rate on this variable. Later, subsequent investigators proposed other intermediate steps involving the formation of ferrous-ferric hydroxide species (7)(8).

Ground waters usually contain a high concentration of  $\text{CO}_2$ . In addition to adding oxygen to water for the oxidation of ferrous iron, aeration has the advantage of removing  $\text{CO}_2$  resulting in an increase in pH. The rate of oxidation of ferrous iron increases rapidly at a pH of 7.0 or above (9)(10).

In practice, oxygen is added to raw waters through aeration. This may be accomplished by:

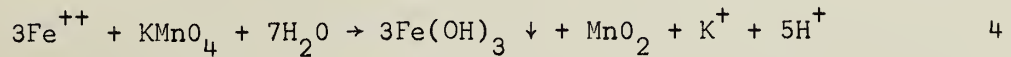
1. open devices over which water flows by gravity, with or without counter-current forced draft, e.g., coke trays, slat trays,
2. spray devices which spray the water into the air,
3. diffused aeration, and
4. aspirator devices, e.g., Venturi devices.

By far, the most common method of aeration, at least in Illinois, is the coke tray aerator. The aerator is usually followed by a reaction or settling basin, prior to the filter.

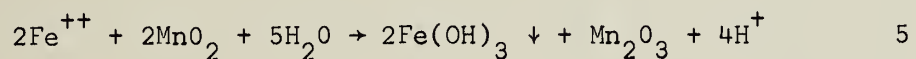
Chlorine or hypochlorites are also effective oxidizing agents and have been used to oxidize iron to the insoluble form (9)(11)(12). Stoichiometrically, 1 mg/l of chlorine will oxidize 1.6 mg/l of ferrous iron.



However, more than theoretical quantities are usually required in practice. Oxidation of iron may be accomplished by using potassium permanganate,  $\text{KMnO}_4$  (13). The reaction may be represented as:



Theoretically, 1 mg/l  $\text{KMnO}_4$  will oxidize 1.06 mg/l of ferrous iron. In practice, however, less  $\text{KMnO}_4$  is required than the theoretical amount. It is believed that this is due to the formation of  $\text{MnO}_2$ , which enters into a catalytic oxidation reaction:



#### 1.4 Unit Processes for Iron Removal

The most common method of iron removal from ground waters involves three basic unit processes, namely, oxidation, settling, and filtration. Once the soluble ferrous iron has been oxidized to the insoluble ferric form by one of the methods described in Section 1.3, it is then partially removed by settling with the remainder being removed by sand filtration. Problems have been encountered in the removal of iron by this conventional method. In an effort to solve these problems to meet the increasing demand for better quality water, various modifications of the conventional method have been tried, as well as entirely different methods. Applebaum et al. (14), Babcock (15), Fosnot (16), Longley (17), and others have discussed the more common methods of iron removal which include:

1. Aeration followed by filtration.
2. Aeration, addition of lime to raise pH, settling and filtration.



3. Same as (2) but with the addition of coagulants in addition to lime.
4. Aeration and filtration through a manganese zeolite bed.
5. Filtration through a sodium zeolite bed without prior aeration.

Recently, it has been suggested that soluble iron can be removed by using magnesite without aeration, followed by filtration on diatomite filters (4).

Van der Wal (18) has reported that iron and manganese are difficult to remove from water by sand filtration without prior floc formation. Babcock (19) reported that settling could be further improved through the use of an upflow clarifier. Because of contact with a previously formed sludge blanket, clarification could be improved. Careful pH control in the range of 8.5 to 9.1 was essential to the formation of a good floc with this type of treatment.

Whatever treatment method is employed, difficulties and incomplete iron removal are often encountered. As early as 1909, Weston (20) reported that organic colloids present in ground waters interfered with the settling of iron. He further noted that certain kinds of organic matter interfered with coagulation of iron when the water was excessively aerated (5). It has been reported by several investigators that this interference is due to the formation of complexes of iron with naturally occurring organic matter or chelation of humic acids with iron (21)(22)(23). However, conclusive evidence is yet to be found to prove this hypothesis.

It has been reported recently that in some plants a reduction of iron from the ferric to the ferrous state occurred during filtration (24) (25). This is always associated with a marked depletion of dissolved oxygen, DO, and a considerable growth of biological slime on the filters.



It has been postulated that the chemical reduction of iron is mediated by the bacterial growth in the filters.

Despite the long period of development and the present widespread use of rapid sand filters, little fundamental information is available concerning the mechanism of iron removal in relation to the biological, chemical and physical equilibria existing in a filter. In most cases design is based on the rules of experience with little or no consideration being given to local conditions. The three most important design factors, namely, the depth of bed, size of sand grains, and the rate of flow, are almost always chosen without reference to factors equally important, e.g., the character of the particles to be removed, the possible development of biological growth, chemical conditions which may affect filtration, and the requisite quality of the filtered water.

Generally the criteria used for the design of iron removal treatment plants are based on empirical observations. Once selected, these criteria are applied to a wide variety of waters indiscriminately without regard to the chemical composition of the particular water involved. Where plants fail to operate satisfactorily, modifications of the treatment units or of the operation are made until by trial and error, satisfactory results are obtained.

### 1.5 Scope of the Present Work

In view of the preceding discussion, it is quite apparent that the existing knowledge in the area of filtration is not adequate in regard to the removal of iron.

Just what causes the depletion of dissolved oxygen associated with the passage of large amounts of iron during filtration reported by



some investigators (24)(25) is not known. It may be hypothesized that the biological growth that occurs in a filter causes a depletion of DO. Such a phenomenon could contribute to the development of an anaerobic and reducing environment in the deeper sections of a conventional 30-inch deep rapid sand filter. If natural waters contain ammonia, microbial nitrification would not only exert an oxygen demand but also cause a lowering of the pH of the water. Thus, low pH values and reducing conditions in a filter would upset the chemical equilibrium in a filter operating normally otherwise. As a result, a reduction of iron from the ferric to the ferrous form and an increase in the solubility of iron may occur.

In the current study, an attempt was made, using natural waters, to determine the influence of biochemical and chemical changes during filtration on the removal of iron. The study, which was conducted with a pilot plant, was carried out at Clinton, Illinois, where problems have been encountered in removing iron. The effect of inhibitors on the bacterial growth in the filters was also studied in an attempt to improve the quality of water with respect to iron.

This study had as its goal the development of a rational method for the engineering design of iron removal plants with proper consideration of the existing local conditions. Another purpose of the study was to determine what remedial measure might be effective in plants which are already in operation but doing an unsatisfactory job of iron removal. The objectives of this study are discussed at length in Section 3.1.



## 2. LITERATURE REVIEW AND THEORETICAL CONSIDERATIONS

### 2.1 Chemistry of Aqueous Iron

#### 2.1.1 Solubility Criteria

The solubility equilibria of ferrous and ferric iron have been discussed extensively by many investigators (26)(27)(28)(29). In natural ground waters, soluble iron exists mainly in the bivalent state. But some ferric iron may also exist in solution especially in aquifers where low pH values are encountered occasionally. A review of the various solubility equilibria of aqueous iron will reveal that when exposed to the atmosphere, natural waters can hold only traces of iron in solution. In the ground, however, natural waters are found to contain much higher quantities of iron in solution than would be predicted theoretically. Two possible reasons have been cited for this discrepancy, namely, non-equilibrium conditions of natural systems with respect to oxygen and formation of iron complexes with various inorganic and organic constituents in natural waters (30)(31).

Figure 1 shows the solubility characteristics of bivalent iron in waters devoid of any species of carbonate or sulfide. In computing the solubilities of ferrous and ferric iron only those equilibria have been considered which are applicable to typical midwestern ground waters. The solubility of  $\text{Fe}^{++}$  is limited by the solubility equilibria of ferrous hydroxide in solid phase,  $\text{Fe}(\text{OH})_2(\text{s})$ . The equilibria represented by Equations 1, 2 and 6 in Table 1 were considered. The species of bivalent iron most expected are  $\text{Fe}^{++}$ ,  $\text{FeOH}^+$  and  $\text{Fe}(\text{OH})_3^-$ . The boundary of the shaded area in the figure defines the maximum solubility of bivalent iron in moles/liter which is expressed as a function of pH in the following relationship,



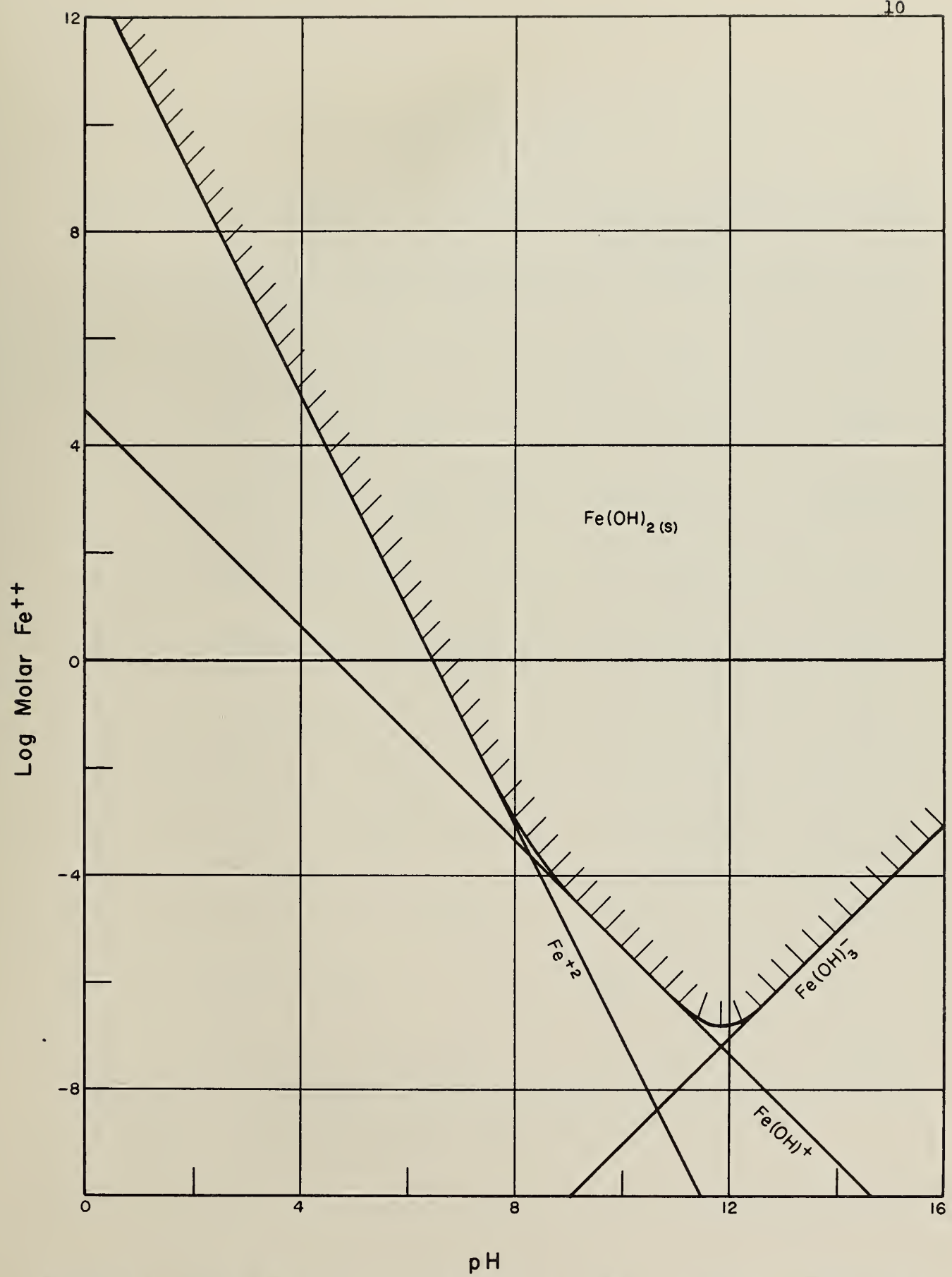


FIGURE 1. SOLUBILITY OF  $\text{Fe(OH)}_2(\text{s})$  IN A NON-CARBONATE, NON-SULFIDE SOLUTION



TABLE 1  
EQUILIBRIA FOR IRON

No.	Equation	Equilibrium constant at 25°C	Reference
1	$\text{Fe(OH)}_{2(s)}^* = \text{Fe}^{+2} + 2\text{OH}^-$	$8 \times 10^{-16}$	(32)
2	$\text{Fe(OH)}_{2(s)} = \text{FeOH}^+ + \text{OH}^-$	$4 \times 10^{-10}$	(32)
3	$\text{FeCO}_{3(s)} = \text{Fe}^{+2} + \text{CO}_3^{=}$	$2.11 \times 10^{-11}$	(33)
4	$\text{FeCO}_{3(s)} + \text{OH}^- = \text{FeOH}^+ + \text{CO}_3^{=}$	$5.05 \times 10^{-6}$	Computed
5	$\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{=}$	$4.7 \times 10^{-11}$	(34)
6	$\text{Fe(OH)}_{2(s)} + \text{OH}^- = \text{Fe(OH)}_3^-$	$8.3 \times 10^{-6}$	(35)
7	$\text{Fe(OH)}_{3(s)} = \text{Fe}^{+3} + 3\text{OH}^-$	$6.6 \times 10^{-38}$	(33)
8	$\text{Fe(OH)}_{3(s)} = \text{Fe(OH)}_2^+ + (\text{OH})^-$	$5.13 \times 10^{-17}$	Computed
9	$\text{Fe(OH)}_{3(s)} = \text{FeOH}^{++} + 2\text{OH}^-$	$2.57 \times 10^{-26}$	Computed
10	$\text{Fe(OH)}_{3(s)} + \text{OH}^- = \text{Fe(OH)}_4^-$	$10^{-5}$	(26)(27)
11	$\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$	$10^{-14}$	
12	$\text{Fe(OH)}_{3(s)} = \text{Fe(OH)}_{3(d)}^{**}$	$2.9 \times 10^{-7}$	(35)

\*  $\text{Fe(OH)}_{2(s)}$  means ferrous hydroxide in solid phase.

\*\*  $\text{Fe(OH)}_{3(d)}$  means undissociated  $\text{Fe(OH)}_3$  in solution.



$$\begin{aligned}
 [\text{Fe}_{(t)}^{++}] &= [\text{Fe}^{++}] + [\text{FeOH}^+] + [\text{Fe}(\text{OH})_3^-] \\
 &= \frac{K_1}{K_w^2} [\text{H}^+]^2 + \frac{K_2}{K_w} [\text{H}^+] + \frac{K_6 K_w}{[\text{H}^+]}
 \end{aligned} \tag{6}$$

where,  $K_1$ ,  $K_2$  and  $K_6$  are the equilibrium constants of Equations 1, 2 and 6, respectively, in Table 1 and  $K_w$  is the ion product of water. The pH range of natural ground waters is within pH 6.0 to 9.0. In such waters, soluble bivalent iron exists mainly as  $\text{Fe}^{++}$  and  $\text{FeOH}^+$ .

Figure 2 shows the solubility characteristics of bivalent iron in alkaline waters. The total alkalinity considered in computing the solubilities was  $10^{-2}$  equivalents/liter (500 mg/l as  $\text{CaCO}_3$ ). In any alkaline natural water, the solubility of bivalent iron is limited by the solubility equilibria of ferrous carbonate,  $\text{FeCO}_{3(s)}$ , up to a pH of 9.0. Above this pH, the solubility equilibria of  $\text{Fe}(\text{OH})_{2(s)}$  (Equations 2 and 6, Table 1) become limiting again. Below a pH of 9.0 the predominant species of bivalent iron are  $\text{Fe}^{++}$  and  $\text{FeOH}^+$  and the maximum possible ferrous iron in moles/liter that can exist in solution, expressed as a function of pH, is given by:

$$[\text{Fe}_{(t)}^{++}] = [\text{Fe}^{++}] + [\text{FeOH}^+] = \frac{[\text{H}^+] + 2K_5}{K_5 \left[ A - \frac{K_w}{[\text{H}^+]} + [\text{H}^+] \right]} \left[ K_3 + \frac{K_4 K_w}{[\text{H}^+]} \right] \tag{7}$$

where, A is the total alkalinity,  $K_3$ ,  $K_4$  and  $K_5$  are the equilibrium constants of Equations 3, 4 and 5, respectively, in Table 1. Under practical conditions pure crystalline solid phases with the given formulas  $\text{Fe}(\text{OH})_2$  or  $\text{FeCO}_3$  are not obtained. The occurrence of basic carbonates, such as the formation of the complex  $[\text{Fe}(\text{OH})_2 \cdot \text{FeCO}_{3(s)}]$  with somewhat different solubility characteristics is probable, especially in the pH range of 8.0 to 11.0 (26).



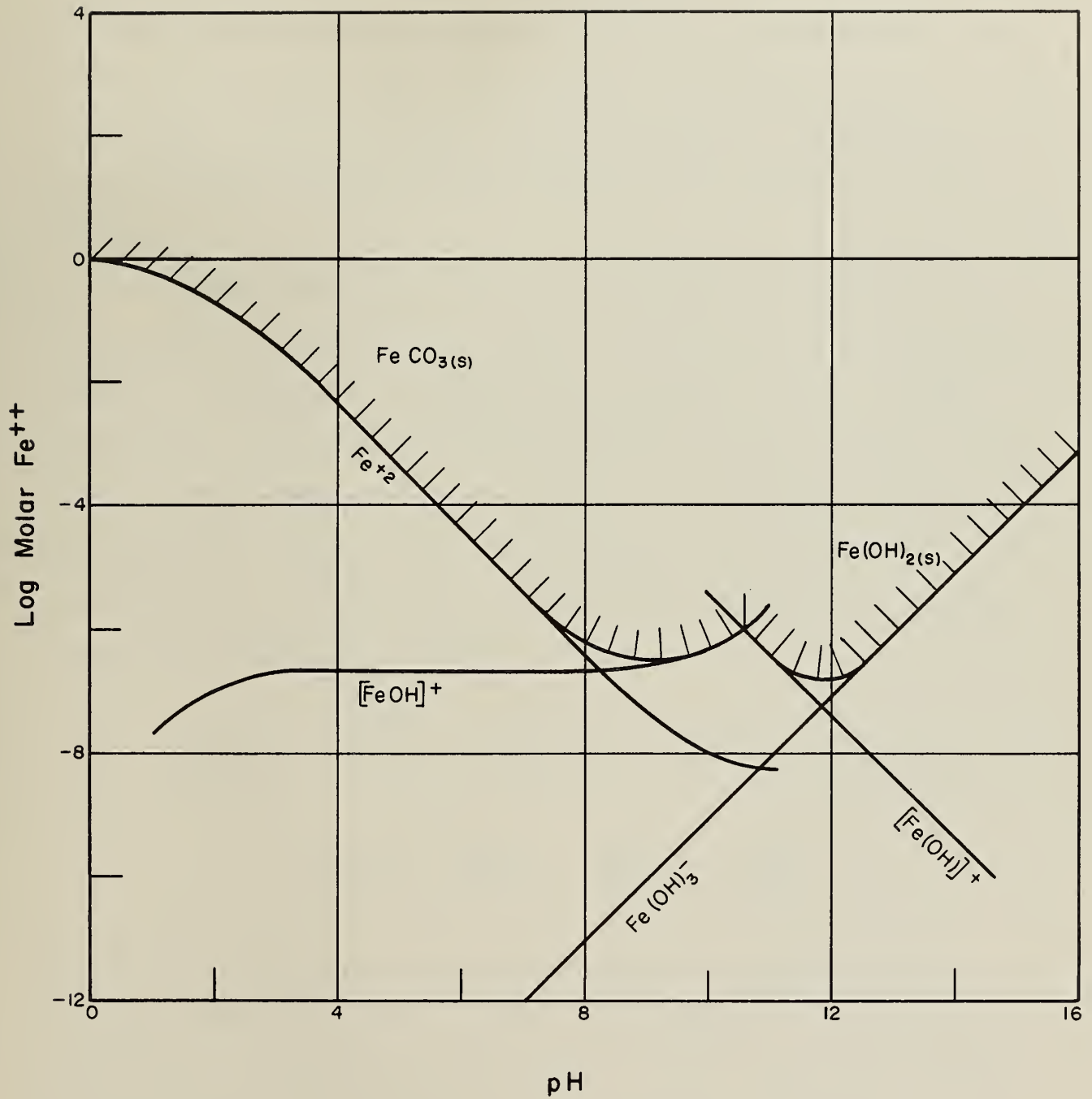


FIGURE 2. SOLUBILITY OF FERROUS IRON IN A CARBONATE-BEARING WATER ( $\text{Alk} = 10^{-2} \text{ eq/l}$ )



A comparison of Figure 1 with 2 indicates that any form of alkalinity reduces the solubility of the bivalent iron considerably. For example, at pH 9.0, the total soluble ferrous iron in a non-carbonate water (Figure 1) is  $5 \times 10^{-5}$  mol/l (2.8 mg/l) whereas in a carbonate bearing water (total alkalinity  $10^{-2}$  eq/l, Figure 2) the solubility is  $3.16 \times 10^{-7}$  mol/l.

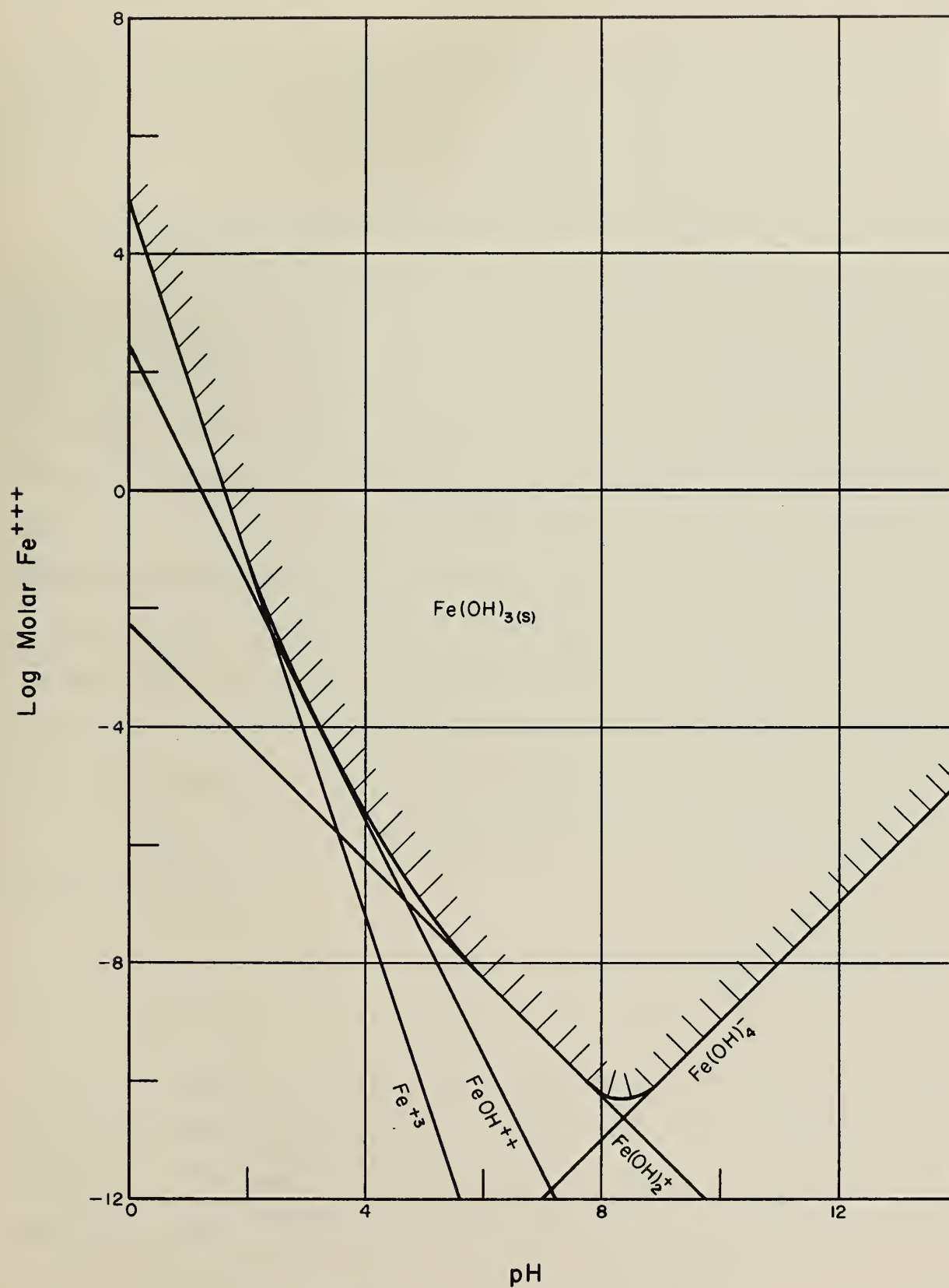
Figure 3 shows the solubility characteristics of trivalent iron. This solubility is limited by the solubility equilibria of ferric hydroxide,  $\text{Fe(OH)}_{3(s)}$ . The species of trivalent iron considered are  $\text{Fe}^{+++}$ ,  $\text{Fe(OH)}_2^+$  and  $\text{Fe(OH)}_4^-$ . The individual solubilities of these species are given by the respective lines whereas the total solubility is given by the boundary of the shaded area. The total solubility was computed using Equations 7, 8, 9 and 10 in Table 1. The solubility in mol/l may be expressed as a function of pH in the following relationship:

$$\begin{aligned} [\text{Fe}_{(t)}^{+++}] &= [\text{Fe}^{+++}] + [\text{Fe(OH)}_2^+] + [\text{FeOH}^{++}] + [\text{Fe(OH)}_4^-] \\ &= \frac{K_7}{K_w^3} [\text{H}^+]^3 + \frac{K_8}{K_w} [\text{H}^+] + \frac{K_9}{K_w^2} [\text{H}^+]^2 + \frac{K_4 K_w}{[\text{H}^+]} \end{aligned} \quad 8$$

The intrinsic solubility or the solution concentration of undissociated  $\text{Fe(OH)}_{3(s)}$  shown by Equation 15 in Table 1 was neglected in these calculations because this species is not in ionic form. The solubility of ferric iron may, however, be much higher if it is complexed with organic or inorganic ligands other than the hydroxyl group,  $\text{OH}^-$ . The formation of chelates, polynuclear species and hydroxo complexes was not considered in constructing the solubility diagrams.

At a pH of 9.0 the concentration of total trivalent iron that can



FIGURE 3. SOLUBILITY OF  $\text{Fe(OH)}_3(\text{s})$ 

Metz Reference Room  
University of Illinois  
B106 NCEL  
208 N. Romine Street  
Urbana, Illinois 61801

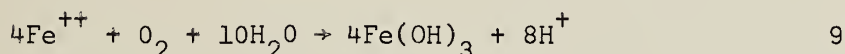


exist in saturation equilibrium with  $\text{Fe}(\text{OH})_3(\text{s})$  is  $10^{-10}$  mol/l ( $5.6 \times 10^{-6}$  mg/l).

### 2.1.2 Oxidation Kinetics of Ferrous Iron

Extensive research has been done to date to determine the factors which influence the kinetics of the oxidation of ferrous iron and those which induce the coagulation and precipitation of oxidized iron and its various hydroxo complexes. The complex equilibrium balance among the various constituents in a natural ground water is not fully understood even today. As a result research in this area has been confined to hypothetical experiments using simulated natural waters prepared in the laboratory. Due to the inadequacies of this type of investigation, only limited application has been found in practice. However, the comparison between natural systems and their idealized counterparts is an essential prerequisite to isolate the variables responsible for observed natural relations.

The basic equation describing the oxidation of ferrous iron by oxygen is given by:



The earliest quantitative investigation on the rate of oxidation of ferrous iron in bicarbonate waters was done by Just (36)(37). He postulated that the rate was first order with respect to ferrous iron and oxygen and second order with respect to  $\text{CO}_2$  as shown in the following relationship:

$$-\frac{d[\text{Fe}(\text{HCO}_3)_2]}{dt} = k \frac{[\text{Fe}(\text{HCO}_3)_2][\text{O}_2]}{[\text{CO}_2]^2} \quad 10$$



He further stated the relationship between the rate and pH as shown below.

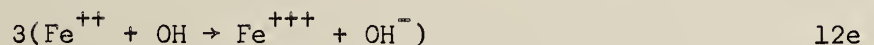
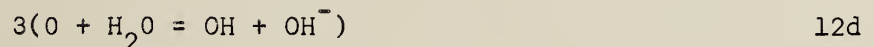
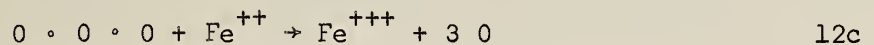
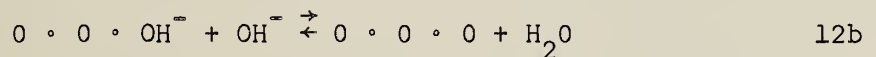
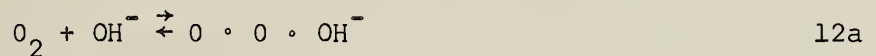
$$-\frac{d[\text{Fe}^{++}]}{dt} = k \cdot \frac{[\text{Fe}^{++}][\text{O}_2]}{[\text{H}^+]^2} \quad 10a$$

He concluded that rate of oxidation increased with  $\text{HCO}_3^-$  ion concentration, but decreased with concentration of free  $\text{CO}_2$ . The kinetics of oxidation postulated by Holluta (33) was given by:

$$\frac{d[\text{Fe}^{+++}]}{dt} = k[\text{Fe}^{++}][\text{O}_2] \quad 11$$

where,  $k$  is strongly dependent on pH.

Abel (38) explained the complicated process of this reaction in a buffered medium by establishing a reaction sequence which is given in Equations 12a to 12e, and which leads to Equation 13 analogous to Equation 10a.



$$-\frac{d[\text{Fe}^{++}]}{dt} = k[\text{Fe}^{++}][\text{O} \cdot \text{O} \cdot \text{O}] = k[\text{Fe}^{++}][\text{O}_2][\text{OH}^-]^2 \quad 13$$



Stumm and Lee (30) established an equation for the kinetics of oxidation of ferrous iron identical to Equation 13 in their work with highly alkaline solutions.

If, during the oxidation and hydrolysis process, the hydrogen ion concentration is constant (which can be virtually reached in well buffered or strongly acidic solutions) in water of a constant oxygen concentration, the oxidation process can be described by the following modified form of Equation 10a,

$$[\text{Fe}^{++}]_t = [\text{Fe}^{++}]_o \cdot \exp. \left( -k \cdot \frac{[\text{O}_2]_t}{[\text{H}^+]^2} \right) \quad 14$$

where,  $[\text{Fe}^{++}]_o$  = initial ferrous iron concentration,

$[\text{Fe}^{++}]_t$  = ferrous iron concentration at time t.

If, during the oxidation process, there is no supply of oxygen to keep the oxygen concentration constant, Equation 10a should be corrected for the amount of oxygen consumed during the process. The modified form of Equation 10a will then be:

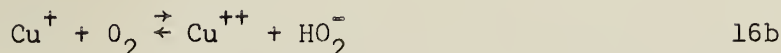
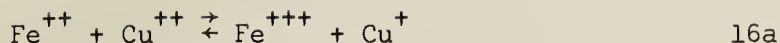
$$-\frac{d(\text{Fe}^{++})}{dt} = k \cdot \frac{[\text{Fe}^{++}]}{[\text{H}^+]^2} \left( [\text{O}_2]_o - 1/4 \cdot \Delta[\text{Fe}^{++}] \right) \quad 15$$

where,  $[\text{O}_2]_o$  = initial oxygen concentration, and

$$\Delta[\text{Fe}^{++}] = [\text{Fe}^{++}]_o - [\text{Fe}^{++}]_t.$$

The use of several cations has been investigated relative to their catalytic effect on the rate of oxidation. The effect of cupric ion on the rate of oxidation of ferrous iron in acid solutions has been studied by Cher and Davidson (39). They postulated the following mechanism:





From these equations, they concluded that a trace amount of copper could initiate a self-sustaining reaction leading to oxidation of ferrous iron. The step inhibiting such a chain reaction could not be postulated from their data. The  $\text{HO}_2^{-}$  formed may further react with  $\text{Fe}^{++}$  as in the Weiss mechanism (Equation 3) (30). Laboratory results suggested that other metal ions,  $\text{Mn}^{++}$  and  $\text{Co}^{++}$ , may also be effective catalysts. The anion  $\text{H}_2\text{PO}_4^{-}$  also has been reported to increase the rate of ferrous iron oxidation (39).

### 2.1.3 The Significance of Redox Potential

The natural environment contains so many variables that it may seem impossible to ascribe any limit to it. However, two components, electrons and protons, are omnipresent in a natural system. Their concentrations, or more precisely their activities, can be measured electrometrically as oxidation-reduction potential and pH respectively. These activities may be plotted one against the other in an  $E_h$ -pH diagram.

The construction of  $E_h$ -pH diagrams for iron was first described by Pourbaix (40). The construction of such diagrams is based entirely on thermodynamic data. The thermodynamic relationships used in computing the standard potential,  $E_o$ , of any chemically reversible electrode reaction are given by:

$$E_h = E_o + \frac{RT}{nF} \cdot \log \frac{a_{\text{ox}}}{a_{\text{red}}} \quad 17$$



$$\text{and} \quad \Delta F^\circ = -nFE^\circ = RT \ln K \quad 18$$

where,  $\Delta F^\circ$  = free energy change

$n$  = number of electrons

$F$  = Faraday

$E^\circ$  = standard electrode potential

$K$  = equilibrium constant

In essence, the oxidation-reduction potential (redox potential) measures the intensity of relative oxidizing or reducing capacity of oxidants or reductants. This potential is a characteristic property of any reversible redox system in thermodynamic equilibrium.

Figure 4 shows the  $E_h$ -pH diagram for the  $Fe^{++} - Fe^{+++}$  system in the natural ground water at Clinton, Illinois. The total activity of soluble iron,  $a_{Fe}$ , and the total alkalinity of this water are  $4 \times 10^{-5}$  moles per liter and  $10^{-2}$  equivalents per liter (500 mg/l as  $CaCO_3$ ), respectively. These values were used in constructing the  $E_h$ -pH diagram. The reactions and equilibria considered in constructing this diagram are listed in Table 2. In all the redox reactions the oxidant together with the required number of electrons are placed on the left of the equations in Table 2. The pH zone in which each reaction or group of reactions occurs is also indicated in the table. The method described by Delahay et al. (41) was used in constructing this diagram and the thermodynamic information was obtained for the most part from Latimer (33) and Pourbaix (40).

The numbers on the lines of the stability-field diagram correspond to the respective equations in Table 2. Each boundary line of the shaded area represents an equilibrium between a solid and an ionic phase. The total activity of soluble iron at any point on these lines is  $4 \times 10^{-5}$  mol/l



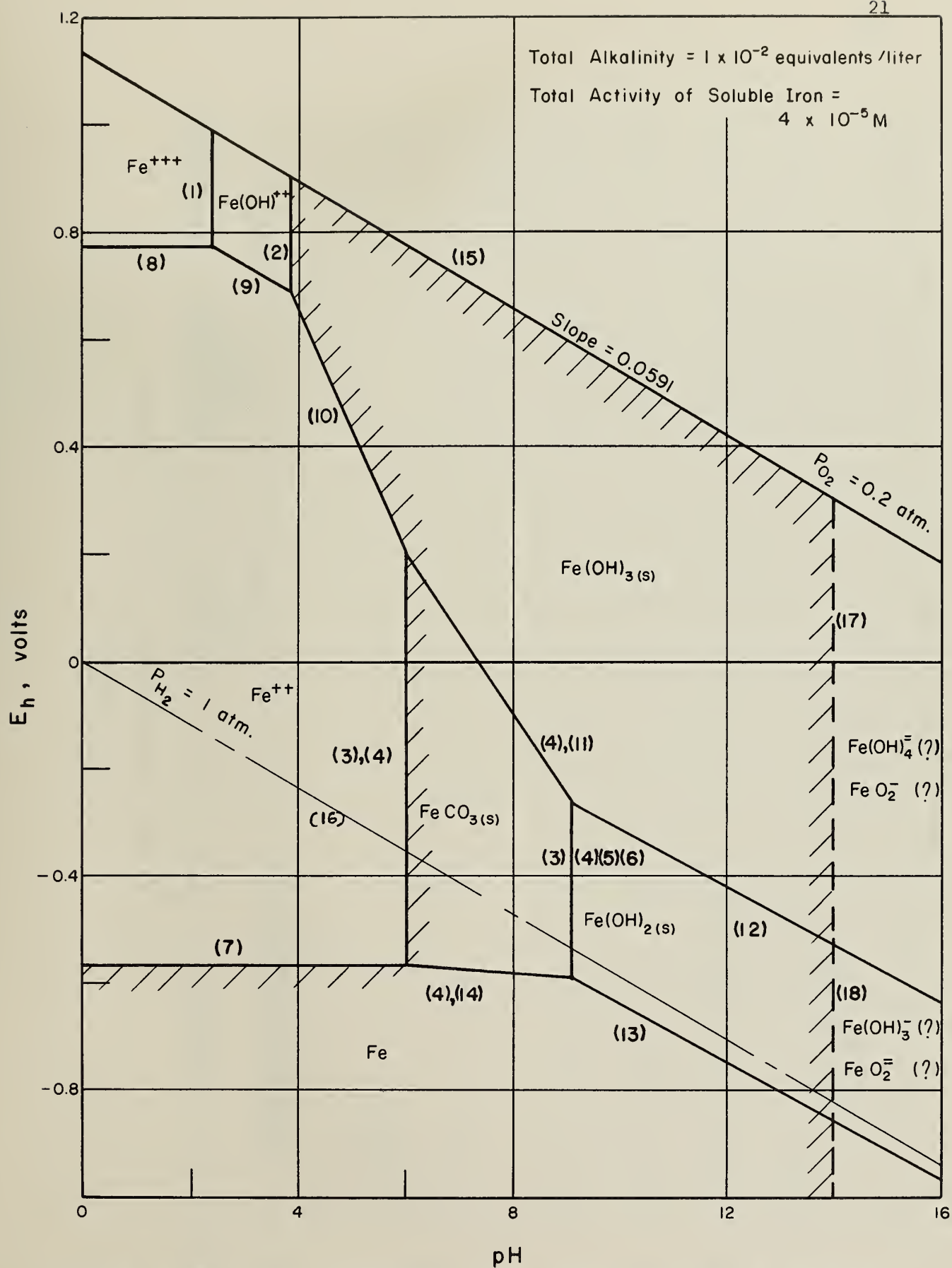


FIGURE 4. E<sub>h</sub> - pH DIAGRAM FOR THE NATURAL WATER AT CLINTON, ILLINOIS



TABLE 2

REDOX EQUILIBRIA FOR IRON-WATER AND  $H_2-H_2O-O_2$  SYSTEMS

No.	Equation	pH zone of influence	Equilibrium constant, 25°C	Reference
<u>Non-Oxidative Equilibria</u>				
1	$FeOH^{++} + H^+ = Fe^{+++} + H_2O;$ $\log \frac{a_{Fe^{++}}}{a_{FeOH^{++}}} = 2.43 - pH$			Computed
2	$Fe(OH)_3(s) + 2H^+ = FeOH^{++} + H_2O;$ $\log a_{FeOH^{++}} = 2.41 - 2pH$			Computed
3	$FeCO_3(s) = Fe^{++} + CO_3^{=}$		$2.11 \times 10^{-11}$	(33)
4	$HCO_3^- = H^+ + CO_3^{=}$		$4.69 \times 10^{-11}$	(34)
5	$Fe(OH)_2(s) + H^+ = FeOH^+ + H_2O$		$4 \times 10^{-10}$	(32)
6	$FeCO_3(s) + OH^- = FeOH^+ + CO_3^{=}$		$5.05 \times 10^{-6}$	Computed
7	<u>Redox Equilibria</u> $Fe^{++} + 2e^- = Fe;$ $E_h = -0.440 + 0.0295 \log Fe$			Computed



TABLE 2 (cont.)

REDOX EQUILIBRIA FOR IRON-WATER AND  $\text{H}_2\text{-H}_2\text{O-0}_2$  SYSTEMS

No.	Equation	pH zone of influence	Equilibrium constant, 25°C	Reference
8	$\text{Fe}^{+++} + \text{e}^- = \text{Fe}^{++};$ $E_h = 0.771 + 0.0591 \log \frac{a_{\text{Fe}^{+++}}}{a_{\text{Fe}^{++}}}$			Computed
9	$\text{Fe}(\text{OH})_2(\text{s}) + \text{H}^+ + \text{e}^- = \text{Fe}^{++} + \text{H}_2\text{O};$ $E_h = 0.915 + 0.0591 \text{ pH} + 0.0591 \log \frac{a_{\text{FeOH}^{++}}}{a_{\text{Fe}^{++}}}$	2.43-3.90		Computed
10	$\text{Fe}(\text{OH})_3(\text{s}) + 3\text{H}^+ + \text{e}^- = \text{Fe}^{++} + 3\text{H}_2\text{O};$ $E_h = 1.06 - 0.1773 \text{ pH} - 0.0591 \log a_{\text{Fe}^{++}}$	3.90-6.05		Computed
11	$\text{Fe}(\text{OH})_3(\text{s}) + \text{CO}_3^{= } + 3\text{H}^+ + \text{e}^- = \text{FeCO}_3(\text{s}) + 3\text{H}_2\text{O};$ $E_o = -0.672$	6.05-9.10		Computed
12	$\text{Fe}(\text{OH})_3(\text{s}) + \text{H}^+ + \text{e}^- = \text{Fe}(\text{OH})_2(\text{s}) + \text{H}_2\text{O};$ $E_h = 0.271 - 0.0591 \text{ pH}$	9.10-?		Computed



TABLE 2 (cont.)  
 REDOX EQUILIBRIA FOR IRON-WATER AND  $H_2$ - $H_2O$ - $O_2$  SYSTEMS

No.	Equation	pH zone of influence	Equilibrium constant, 25°C	Reference
13	$Fe(OH)_2(s) + 2H^+ + 2e^- = Fe + 2H_2O;$			
	$E_h = 0.0475 - 0.0591 \text{ pH}$	9.10-?		Computed
14	$FeCO_3(s) + 2e^- = Fe + CO_3^{=}$			
	$E_o = -0.756$	6.05-9.10		Computed
15	$O_2 + 4H^+ + \frac{O_2-H_2O \text{ System}}{4e^-} = 2H_2O;$			
	$E_h = 1.229 - 0.0591 \text{ pH} + 0.0148 \log (P_{O_2})$			Computed
16	$2H^+ + 2e^- = H_2;$ $\frac{H^+-H_2 \text{ System}}{2e^-}$			
	$E_h = -0.0591 \text{ pH} - 0.0295 \log (P_{H_2})$			Computed



(2.23 mg/l). Lines 1, 8 and 9 represent equilibria between two ionic phases. The activity ratio of two ions, e.g.,  $\frac{a_{\text{Fe}^{+++}}}{a_{\text{Fe}^{++}}}$  on line 8, is unity. The rest of the lines denote equilibria between two solid phases. Thus, the activity of soluble iron is less than  $4 \times 10^{-5}$  mol/l in the shaded area whereas in the unshaded region the concentration is more than  $4 \times 10^{-5}$  mol/l. In the region bounded by line 1 and line 8,  $\frac{a_{\text{Fe}^{+++}}}{a_{\text{Fe}^{++}}}$  is more than one. It can also be seen that in this water it is possible to precipitate  $\text{FeCO}_3(\text{s})$  at pH values between 6.0 to 9.0 even at negative potentials. At a pH of 7.0, for example,  $\text{FeCO}_3(\text{s})$  is thermodynamically stable between potentials -0.575 to +0.050 volts. It would seem quite possible to precipitate all soluble  $\text{Fe}^{++}$  iron as  $\text{FeCO}_3(\text{s})$  in this water. By raising the potential above +0.050 volts at a pH of 7.0, it is possible to oxidize  $\text{Fe}^{++}$  iron to  $\text{Fe}^{+++}$  form and to precipitate it as  $\text{Fe}(\text{OH})_3(\text{s})$ . Therefore, the kinetics of oxidation and precipitation would determine the relative proportions of  $\text{FeCO}_3(\text{s})$  and  $\text{Fe}(\text{OH})_3(\text{s})$  to be expected in the solid phase in this system. Due to the lack of sufficient and reliable thermodynamic data for the iron-water system in highly alkaline regions, pH 10.0 or higher, lines 12, 13, 17 and 18 cannot be accurately predicted. It is believed that ferrite ( $\text{FeO}_2^-$ ), hypoferrite ( $\text{FeO}_2^=$ ),  $\text{Fe}(\text{OH})_4^-$  and  $\text{Fe}(\text{OH})_3^-$  ions may exist at these pH values, depending on the  $E_h$  of the system.

The  $E_h$ -pH diagram can be of significant value in interpreting observations made in the field. However, this is strictly a theoretical diagram and should be regarded as such. The accuracy of pH determination, salt effects on pH values, existence of other redox equilibria besides  $\text{Fe}^{++} - \text{Fe}^{+++}$ , e.g.,  $\text{SO}_4^{=} - \text{S}^{=}$ ,  $\text{NH}_4^+ - \text{NO}_2^- - \text{NO}_3^-$ ,  $\text{Cu}^{++} - \text{Cu}^+$ , etc., causing a "mixed" potential, will influence the observed  $E_h$  values of a natural Fe -  $\text{H}_2\text{O}$  system. These uncertainties may account for discrepancies observed



between theoretical and observed  $E_h$  values and between the theoretical and observed solubilities. Overall, the  $E_h$ -pH diagram does provide a model which helps to explain natural systems on a theoretical basis.

In most iron removal plants, such as the one at Clinton, the water is either exposed to the atmosphere representing an infinite source of oxygen at a fixed partial pressure,  $P_{O_2}$ , of approximately 0.2 atmosphere or is generally saturated with  $O_2$  at constant  $P_{O_2}$  by aeration. The solubility of oxygen in water obeys Henry's law. This may be written as:

$$[O_2] = k P_{O_2} \quad 19$$

The dissolved oxygen will react with the reduced forms of iron present in the water. But because the oxygen source is unlimited, it is obvious that the redox potential of any water system is determined by the partial pressure of oxygen as long as the system is in equilibrium with the atmosphere. All other redox couples,  $Fe(OH)_3 - Fe^{++}$  for example, will be adjusted at equilibrium in such a way that the ratio of their activities corresponds to the redox potential of the  $O_2 - H_2O$  couple. Line 15 in Figure 4 represents the  $E_h$ -pH relationship for  $O_2 - H_2O$  water couple. This is obtained from the Peter-Nernst equation (Equation 15, Table 2). On the other hand, the  $E_h$ -pH relationship for the couple  $H^+ - H_2$  is shown by line 16 (reaction 16, Table 2). Thus, water is stable between lines 15 and 16. Above line 15, water is oxidized while below line 16, water is reduced. It can be seen that for both of these couples,  $E_h$  changes by 0.059 volts for each unit change of pH at any given partial pressure of the gaseous phase ( $O_2, H_2$ ). The change in  $E_h$  due to a change in  $P_{O_2}$  or  $P_{H_2}$  is quite insignificant.



The iron-oxygen-water system also must be considered. The basic process of the oxygenation of  $\text{Fe}^{++}$  iron is given by the chemical equilibrium represented in Equation 9.  $E_o$  for this equilibrium is calculated from the standard free energy values for the products and reactants as shown below:

	$\Delta F^\circ$ , Kcal/mole
$\text{Fe}^{++}_{(\text{aq})}$	= - 20.3
$\text{H}_2\text{O}$	= - 56.69
$\text{Fe}(\text{OH})_{3(\text{s})}$	= -166.0

$$E_o = \frac{\Delta F^\circ}{nF} = \frac{-4 \times 20.3 - 10 \times 56.69 + 4 \times 166.0}{4 \times 23.07}$$

where,  $F = 23.07 \frac{\text{Kcals}}{\text{volt}}$

$n$  = number of electrons involved in the reaction.

Therefore,  $E_o = 0.172$  volt. Thus, the  $E_h$ -pH relationship will be (oxygen non-limiting):

$$\begin{aligned}
 E_h &= E_o + \frac{RT}{nF} = \log \frac{[\text{H}^+]^8}{[\text{Fe}^{++}]^4 [\text{P}_{\text{O}_2}]} \\
 &= 0.172 + \frac{0.0591}{4} (-8 \text{ pH} - 4 \log [\text{Fe}^{++}] - \log \text{P}_{\text{O}_2}) \\
 &= 0.172 - 0.0148 (8 \text{ pH} + 4 \log [\text{Fe}^{++}] + \log \text{P}_{\text{O}_2}) \quad 20
 \end{aligned}$$

From his study with central Illinois ground waters, Goswami (42) calculated  $E_o$  from observed  $E_h$  data and found it to be +2.90 volts. This was based on



total  $[\text{Fe}^{++}]$ , soluble and insoluble. Larson (43) modified this value by using soluble  $[\text{Fe}^{++}]$  iron values and found  $E_o$  to be between +1.439 to +1.560 volts. The discrepancy between the theoretical and observed values seems to be due to the influence of other redox systems and the existence of non-equilibrium conditions in natural waters. Thus, it appears that  $E_h$  values for natural systems represent mixed potentials. Under such conditions no measured  $E_h$  value can be interpreted in terms of a simple half reaction as shown in Equation 20.

## 2.2 Coagulation and Sedimentation of Insoluble Iron

In the pH range of natural waters (6.0 - 9.0), having alkalinity values between 400 mg/l to 500 mg/l as  $\text{CaCO}_3$ , it is possible to precipitate bivalent iron as  $\text{FeCO}_3$  along with the more common trivalent form,  $\text{Fe}(\text{OH})_3$ . Recently, it has been reported by O'Connor, Ghosh and Engelbrecht (44) that in central Illinois ground waters the rate of iron precipitation is governed by the alkalinity and pH of the water as shown by the following relationship:

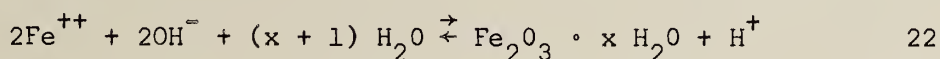
$$T_{1/2} = 522 - 0.33 \times 10^{14} [\text{OH}^-]^2 - 183 \cdot \log [\text{A}] \pm 8.10 \quad 21$$

where,  $T_{1/2}$  = half-life in minutes

$[\text{OH}^-]$  = molar concentration of hydroxyl ion

$[\text{A}]$  = alkalinity in mg/l as  $\text{CaCO}_3$

The ferric iron formed due to the oxidation of ferrous iron is hydrolyzed according to the equation:





The insoluble ferric oxide hydrate can exist in two forms, namely, the sol form (stable) and the floc form (unstable). Sol particles can grow to larger agglomerates, i.e., flocs. Both forms will be present after hydrolysis. However, it is apparent that flocculated particles are more easily filterable than the sol particles. Heertjes and Lerk (45) reported,

".....the sol particles offer much more resistance to filtration than the flocs. ....The best method (to alleviate this problem) would be to prevent the formation of sol particles altogether, and such measures have to be employed during aeration process."

It is, however, possible that in waters rich in organic material, colloidal ferric oxide hydrate is stabilized as a sol protected by organic compounds (46). Complex formation in solution by replacing the molecules in the solvate shell of the free metal cation by other ligands may increase the solubility of insoluble iron ( $\text{Fe}^{++}$  and  $\text{Fe}^{+++}$ ) (47).

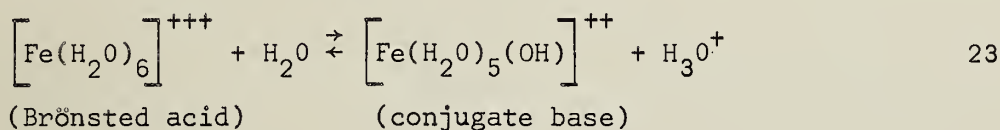
The possible sources of interference in the removal of iron by aeration and sedimentation, as enumerated by Robinson (48), were:

1. the formation of soluble hydroxo polymers of aquo bases of iron,
2. the formation of colloidal dispersions with organic colloids, and
3. the formation of soluble chelates with organic sequestering agents.

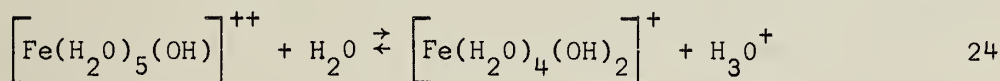
The basic step in the formation of hydroxo polymers of any metal is a stepwise hydrolysis. For ferrous iron, the most common hydrolysis products that may exist in natural water are  $[\text{Fe}(\text{H}_2\text{O})_6]^{++}$ ,  $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^+$ ,  $\text{Fe}(\text{OH})_2$  and  $[\text{Fe}(\text{H}_2\text{O})_3(\text{OH})_3]^-$  (32)(35). For brevity  $\text{H}_2\text{O}$  ligands are generally omitted from the chemical formulae for these species. For ferric iron, the most common hydrolysis products are  $\text{FeOH}^{++}$ ,  $\text{Fe}(\text{OH})_2^+$ ,  $\text{Fe}(\text{OH})_3$ , and  $\text{Fe}(\text{OH})_4^-$ . The concept of hydrolysis, or, in the Brönsted terminology, acidity of hydrated metal ions, can be conveniently used in discussing the complex



ions. Since aquo ferric ion has far more affinity toward hydrolysis than the aquo ferrous ion, this discussion will be limited to hydrolytic reactions of aquo ferric iron only. The acid-base equilibrium for ferric iron may be expressed as:

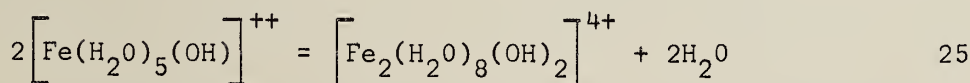


The process involves the substitution of a proton for a coordinated  $\text{H}_2\text{O}$  molecule converting it to a hydroxide. The conjugate base,  $\left[ \text{Fe}(\text{H}_2\text{O})_5(\text{OH}) \right]^{++}$ , of Equation 23 can be further protonated to yield the second conjugate base:



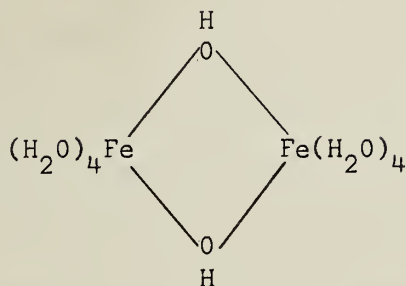
Thus, these hydrolytic reactions will progress until the formation of the aquo base  $\text{Fe}(\text{OH})_4^-$ . The acidity constant of Equation 23 is quite high ( $K = 6.78 \times 10^{-3}$ ). Thus, it is evident that the use of any iron salt, e.g.,  $\text{FeCl}_3$ , for coagulating insoluble iron will only result in a decrease in pH and thereby an increase in the solubility of all the insoluble species of iron in the aerated water.

Ferric hydroxo complexes have been known to polymerize. Such phenomena were first reported by Thomas (49)(50). It was shown that iron atoms are bound by "diol" (dihydroxy) bridges in the polymer state, attained through "olation" reactions. An example is shown below:

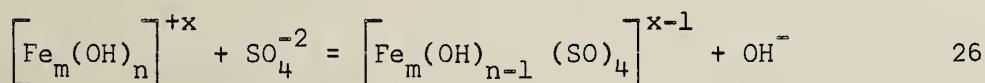




The probable structure for the above dimer is:



Thus, metastable colloidal iron hydroxo polymers are formed through hydrolysis and polymerization. In the acid to neutral pH range, positively charged colloidal ferric oxide is formed while in the alkaline range negatively charged colloidal ferric oxide prevails. It has been reported by Stumm and Morgan (51) that in a  $10^{-3}$  M ferric iron solution, 20 percent of the ferric species exist as  $\text{Fe}^{+++}$ . The balance is made up of 40 percent  $\text{Fe}(\text{OH})^{++}$ , 5 percent  $\text{Fe}(\text{OH})_2^+$ , and 35 percent  $\text{Fe}_2(\text{OH})_2^{4+}$ . In more concentrated solutions, the tetrapositive dimer is the predominant product of protonation. The positively charged ferric oxides are hydrophobic in nature. However, these may be stabilized by a coating of hydrophilic negatively charged colloids in natural waters and thus carry a net negative charge. Perikinetic coagulation of such colloids may be effected by reducing the zeta potential. This can be done by destabilization of the sol with multivalent ions or colloids of opposite charge of that on the sol. The mechanism of this destabilization is mainly by ligand exchange reactions of the type shown below with a resultant increase in pH:



The coagulant ions form a complex with colloidal ferric oxide hydrate.



However, a certain degree of adsorption of such ions on the colloid may be expected (26). Once the sol is destabilized, flocculation is then initiated resulting in gravity sedimentation of the insoluble iron.

Riddick (52)(53)(54) has discussed in detail the methods for measuring the zeta potential in natural waters. He reported that a zeta potential of +5 mvolts to be optimum for the removal of all naturally occurring colloids, including those of iron. In order to attain such low potentials, the alkalinity in the water should be slightly in excess of that stoichiometrically required to react with the coagulant. Riddick suggested the use of a coagulant dosage sufficient to lower the zeta potential to -10 mvolts, provided that at least 6 to 8 mg/l of alkalinity remained. A suitable coagulant aid or cationic polyelectrolyte then is added to raise the potential to zero.

A great deal has been published about difficulties in iron removal from waters having a high content of organic matter. Some investigators have proposed that the iron or some part of the total iron content does not flocculate because it is organically chelated. Another theory is that the colloidal organic matter will act as a protective agent in regard to the flocculation of the iron. The latter theory has already been discussed. However, it may be added that destabilization of such colloidal organic matter can sometimes be achieved by a slight pH adjustment.

## 2.3 Filtration

### 2.3.1 Mechanism of Filtration

Numerous experiments and studies have been conducted, during the past 40 years, on the mechanism of filtration. These studies, for the most part, have been confined to the hydraulics of the process. Many of these



studies have had as their goal the development of filters with higher efficiency of removal and with longer periods of filtration. Improvements have been made in the design of rapid sand filters by modifying the filter media and selecting optimum rates of filtration. However, very few reports are available on the performance of a filter in relation to iron removal and the biochemical equilibria that exist in a filter.

Various materials can be used as effective filtering media. The most durable and, perhaps, the cheapest material available is sand. At one time, the gravity type slow sand filters were most common. However, in the course of time, these have been replaced by rapid sand filters of either the gravity or pressure type.

The increase in filtration rates resulting from the change from the old slow sand filters to the rapid sand filters was such an improvement that for many years no one considered the possibility that a further increase in the rate of filtration was still possible. In the 1930's research was undertaken for the first time to investigate if higher rates of filtration were acceptable without any detriment to the quality of water and without any change in the economy of the process. Baylis (55)(56) was the first to suggest such a change. In the Chicago Experimental Filtration Plant, water of acceptable quality could be produced employing rates as high as 5 gpm/sq ft during periods of "strong coagulation." An increase in the rate from 1.6 to 3.5 gpm/sq ft increased the effluent turbidity from 0.06 to 0.09 units and the bacterial count from 3.5 per 100 ml to only 5.6 per 100 ml. Using activated silica as a coagulant aid during periods of "weak coagulation," good quality water could be produced at a high rate of 5 gpm/sq ft. On the basis of the test results the length of the filter run in hours was reported as inversely proportional to the 1.5 power of the filtration rate. Deeper



penetration has been suggested as the reason for the higher performance at high rates, but this hypothesis is not supported with experimental evidence.

Filtration of homogenized iron floc particles labelled with a radioactive iodine tracer was studied by Stanley (57). He reported on the reaction of iron floc with a uniform sand bed. In particular, the effect of filtration rate on the penetration of iron floc in filters having sand grains of 0.84-0.59 mm and 0.42-0.29 mm particle diameter was observed. No data were reported on actual iron concentration in the effluent, but the penetration depth was arbitrarily determined as that depth in the bed where the radioactive count was equal to the background count plus one standard deviation. His findings were as follows:

$$\text{Penetration Index (P.I.), cm/mg/cm}^2 = \frac{d}{c} = \text{constant} \quad 27$$

where, d = depth, cm

c = concentration of ferric floc per unit surface area of bed, mg/cm<sup>2</sup>.

The Penetration Index increased with the addition of electrolytes such as NaCl, Na<sub>2</sub>SO<sub>4</sub> and MgSO<sub>4</sub>. It decreased if the floc size was increased or if the floc was aged. The P. I. also shifted with a change in the pH of water. It was at a minimum at the isoelectric point. The following relationship was established for a uniform sand filter operating to a terminal head loss of 8 feet at a temperature of 25°C:

$$l = K d^{2.46} \cdot Q^{1.86} \quad 28$$

where, K = constant = 1850 for an effluent quality of 0.2 mg/l iron (as turbidity)



$l$  = depth of filtering medium, inches

$d$  = dia of sand, cm

$Q$  = rate of flow, gpm/sq ft

It was also found that the time required to build up a head loss of 8 feet was proportional to the 0.6 power of the filtration rate, indicating an improvement in filtration at higher rates.

Hall (58) reported that higher filtration rates resulted in greater penetration of material. Thus, more water may be produced per unit increase in head loss while water quality can be safeguarded using a greater sand depth or a smaller terminal head loss. Filtration rates of 10 gpm/sq ft are possible without deterioration of water quality if the grain size and depth of the medium are properly selected.

### 2.3.2 Theory of Filtration

Early reports on filtration indicated that most of the removal of suspended matter took place near the surface of the sand bed (55). The materials which pass through the surface zone are removed predominantly at the contact points between the sand grains (56)(59). The penetrating material which is removed in any lamina of the filter at a given time is dependent on the material in the influent to this lamina at the moment of filtration. It is not due to the material previously deposited which is being forced deeper into the filter (57)(59). The particles that penetrate deepest are smaller than those arrested at the top of a filter.

Reporting on iron removal by sand filtration, Ling (60) concluded that in a clean filter the iron concentration in the effluent increases with time to a peak value and then decreases rapidly to a minimum level. The time required for filters to reach peak efficiency at the start of a



filtration period was termed the "lag time." Ling believed that this was the time required to form a coating of iron floc on the sand grains. The time at which peak iron concentration was observed in the effluent at the start of a filtration period was approximately equal to the theoretical time for the water to flow through the filter.

Using a pilot pressure sand filter, Holluta and Eberhardt (7) studied the filtration of iron bearing water at rates between 2 and 16 gpm/sq ft to a terminal head loss of 30 to 45 ft. The penetration and precipitation of iron within the filter were investigated using various sand sizes, iron contents and filtration rates. It was observed that the iron being passed by the filter was always in the soluble ferrous form. The precipitated iron was immediately removed on the sand, and no break-through of such iron was noticed even at the very high rates. Therefore, it was concluded that the rate limiting reaction in the removal of iron by aeration and filtration was oxidation of ferrous iron to hydrated ferric oxide floc. The natural logarithm of the effluent iron content was found to be proportional to the time of iron contact within the filter, the time of contact being inversely proportional to the filtration rate. Higher rates resulted in higher effluent iron due to insufficient time of oxidation. On the basis of their observations, Holluta and Eberhardt (7) derived an empirical relationship for the removal of iron from aerated waters by a rapid sand filter. The kinetics of removal were given by:

$$-\frac{d[\text{Fe}^{++}]}{dt} = k_1 k_c [\text{Fe}^{++}] \quad 29$$

This equation was found to be valid for a water where pH was constant (well buffered natural water) and the oxygen content was at the saturation level



(8.5 to 10 mg/l for well aerated natural water).  $k_1$  included the constants due to pH and  $O_2$  and  $k_c$  was the coefficient of catalysis or the surface action of the precipitated ferric oxide hydrate. Integrating Equation 29, the following relationship is obtained:

$$k_1 k_c t = \ln [Fe^{++}]_0 - \ln [Fe^{++}]_t$$

$$\text{or} \quad [Fe^{++}]_t = [Fe^{++}]_0 \cdot e^{-k_1 k_c t} \quad 30$$

where,  $t$  = time of contact of water with sand

$[Fe^{++}]_0$  = initial ferrous iron conc., and

$[Fe^{++}]_t$  = ferrous iron conc. at time 't'

The catalysis that occurs at the surface of the solid iron precipitate makes the rate determining reaction heterogenous. Therefore, the overall removal rate will depend on the area of contact between the water and the solid precipitate, contact time (the flow through time), and the sand size. Thus, the constant  $k_c$  depends upon the contact time ( $t$ ) as determined by the rate of filtration and the sand size which codetermines the catalytic surface.

Studies on the effect of pH on the filtration of iron floc by Stanley (57) indicated that the lowest penetration of floc occurred at the isoelectric point of the suspension. It is known that the hydrogen ion concentration greatly influences the mechanism of coagulation. For the same reason it has been reported to affect the filterability of a floc suspension (61). Stanley reported that particles formed at pH 5.2 were much smaller than those formed at pH 6.8. Thirty-nine percent of the floc passed through the sand filter at a pH of 5.2. The importance of pH in



relation to filtration of iron flocs was summarized by Stanley as follows:

"An H ion is a specific counter ion which neutralizes hydroxyl groups on hydrous ferric oxide floc. This high affinity for the floc produces positively charged particles when sufficient H ions are present. When the particles are broken up in the presence of a large number of H ions, they will not coagulate again as readily, because the resulting high positive charge causes an increase in the electrokinetic repelling forces.....

"This reasoning may also be used in explaining why a large percentage of such floc passes through a sand filter. Clean Ottawa sand grains have negatively charged surfaces. Thus, it would seem that positively charged particles in suspension will be removed readily. This is perhaps true so long as the surface of the filter medium remains negatively charged. However, the small particles in suspension coat the sand grain surfaces very rapidly, producing a charge essentially the same as that on the floc particles in the suspension. The particles would then have the best chance of adhering to one of these surfaces if the electrokinetic forces of repulsion were at a minimum. This occurs at pH values close to the isoelectric point. Thus, the best coagulating floc will also be the best filtering floc. A curve for 'time of floc formation vs. pH' indicated a minimum at about pH 7.0."

Stein (59) reported from his studies that sedimentation is not an important mechanism in filtration. In essence, two mechanisms working cooperatively seem most effective:

- 1) straining both at the surface and at the interstitial cavities within the bed, and

- 2) contact adherence of particles coming in close proximity to sand or previously deposited floc. This is facilitated by the interplay of the electrokinetic forces.

Since the mid 1930's there has been a tendency to use coarser sand in filters which permits deeper penetration of floc and longer filter runs. It is obvious that deeper filters are necessary if coarse sand is used. On the other hand, when fine sand is used, a dense surface mat forms which settles to the bottom during backwashing and thus contributes to the formation



of mud balls (62). The use of coarse sand makes high backwash rates necessary. However, low backwash rates can more effectively clean filters because of greater opportunity for abrasion between sand grains. The studies with high filtration rates have led to the use of sand with an effective size of approximately 0.6 mm.

In 1937, a mathematical evaluation of filtration was proposed by Iwasaki (63). This is still the predominant concept on which the present equations applicable to rapid sand filtration are based. The following equations were developed by Iwasaki:

$$\frac{\partial C}{\partial L} = - \lambda C \quad 31$$

$$\lambda = \lambda_0 + k S \quad 32$$

$$\frac{\partial C}{\partial L} + \frac{\partial S}{\partial y} = 0 \quad 33$$

where, C = concentration of suspended matter in the flow

L = depth of any point in a filter

$\lambda$  = impediment modulus

$\lambda_0$  = initial impediment modulus

k = coefficient of impediment modulus

S = amount of suspended matter arrested

y = filtration time.

Equation 31 states that the amount of suspended matter, e.g., insoluble iron floc, arrested in a given layer of sand is proportional to the concentration of the suspended matter entering the layer.

Equation 32 states that the proportionality factor or the



impediment modulus,  $\lambda$  (length<sup>-1</sup>), changes with time and, as the voids of the filter become filled, the change in  $\lambda$  is directly proportional to the amount of the matter filling the voids.

Equation 33 is a continuity equation. This states that inert matter can neither be created nor destroyed, or that the decrease in concentration of the suspended matter in the flow through a filter lamina is directly accounted for by the increase in the amount of the matter deposited on the lamina in the time required for the water to flow through the lamina.

Generally, it is assumed that the volume of the floc particles remains fairly constant during their passage through the granular sand bed and are deposited on the grains to remain throughout the filtration period; i.e., no breakthrough occurs during filtration. The volume of the floc particles removed from the water will then be equal to the volume deposited in the bed. This relationship was also proposed by Iwasaki (63) as follows:

$$\frac{\partial \sigma}{\partial t} = -v \cdot \frac{\partial C}{\partial L} \quad 34$$

where  $\frac{\partial \sigma}{\partial t}$  denotes the time rate of change of the deposit ratio,  $\sigma$ , at a particular filter depth,  $L$ , and a particular time,  $t$ ;  $\frac{\partial C}{\partial L}$  represents the corresponding rate of decrease in volumetric concentration of floc in water,  $C$ , and  $v$  represents the rate of filtration.

Later, other investigators found that the above equations were fundamentally correct except that  $\lambda$  decreases after an initial increase (57)(59). As the filter becomes clogged the pore velocity increases and the probability of a particle being deposited is minimized.

The latest modification to the basic filtration equations was made by Ives (64) and is shown below:



$$\frac{\partial C}{\partial L} = - (\lambda_o + k_1 \sigma - \frac{\theta \sigma^2}{f_o - \sigma}) C \quad 35$$

where,  $k_1$  = rate factor parameter

$\sigma$  = deposit ratio (volume of deposited solids as percent of filter volume)

$\theta$  = rate factor parameter

$f_o$  = initial porosity of the filter

$\lambda_o$  = initial impediment modulus

$C$  = concentration of suspended solids

$L$  = depth of any point in the filter.

The assumptions made in the development of Equation 35 were:

1) the filter media was isotropic and homogeneous throughout its depth, and

2) the suspended matter consists of discrete, uniform, homogeneously dispersed particles. The assumptions, however, seem inconsistent because in practice such conditions are not normally encountered. Instead, filter sands are well stratified from repeated backwashings.

A theoretical development of the shear force in a filter was produced based on the fact that drag is a function of the Reynold's number and the form of the body. This was eliminated in developing Equation 35. Since suspended matter initially settles at a rate equal to the vector addition of the settling velocity and the flow velocity, and since the flow velocity is a gradually increasing function, it would seem probable that any particle could be deposited and at some later time be sheared off the sand grain if the rate of filtration is held constant. Ignoring shear effects, the modified equation has the form shown in Equation 31.



Cleasby et al. (65) studied the filtration of ferric iron floc having an almost negligible amount of ferrous iron. They reported that the amount of ferric iron in the effluent decreases with increasing depth. In the initial stages, 5 minutes after the beginning of filtration using a clean filter, iron penetrated up to a depth of 20 inches, but as time progressed this depth decreased and the curve showing the amount of iron in the effluent vs. depth was very close to a decreasing exponential curve. In other words, it followed the basic first order kinetics of Equation 31. The influent iron concentration was between 10 and 12 mg/l. But after 142 minutes of operating time at a rate of 4 gpm/sq ft, the effluent iron concentration decreased to 0.2 mg/l even with a filter depth of 10 inches. However, considerable iron was present in the effluent at a depth of 20 inches, 5 minutes after the filtration was started. Cleasby's data indicated an "initial lag" time of 7 minutes at a filtration rate of 4 gpm/sq ft with a peak breakthrough concentration of 1.19 mg/l after filtration had progressed for 7 minutes. However, regardless of the rate of filtration, after about 50 minutes of operation the filter seemed to have attained a state of equilibrium and the concentration of iron in the effluent at a depth of 24 inches was less than 0.3 mg/l. It was observed that the initial "lag period" was dependent on the filtration rate. No reduction of ferric iron to the ferrous form was reported.

### 2.3.3 Biochemical Aspects of Filtration

Very few references in the literature can be found which indicate that the biological growth in a rapid sand filter may be a potential cause for the problems encountered by some plants in removing iron by filtration. Longley (17) and Komolrit (24) indicated that in some plants biological



activity in the filter may be responsible for the reduction of ferric iron to the ferrous form and also for the depletion of dissolved oxygen in the filter. Robinson (25) reported that the actual interference with iron removal was perhaps due to the biological activity which was supported by the humic acids present in natural waters. This biological activity may create reducing conditions which may reconvert precipitated iron to a soluble ferrous form.

Bivalent iron, soluble or insoluble, is thermodynamically unstable in the presence of oxygen or other oxidizing agents and is oxidized to the trivalent state under favorable pH conditions. Trivalent iron may undergo reduction if a suitable reductant is available. For example,  $S^{2-}$  components, which are thermodynamically unstable in the presence of oxygen, are capable of reducing trivalent iron. The tendency of this reaction to take place increases with decreasing pH. Some reducing components, e.g.,  $NO_2^-$ , can be formed through bacterial metabolic processes and may be capable of reducing trivalent iron.

In natural waters reduced organic and inorganic substances prevail only when anaerobic conditions exist. Many of the organic reductants found in natural waters are capable of reducing soluble ferric iron to the ferrous state. The trivalent state of iron may, however, be stabilized to some extent in the presence of complex formers, especially organic bases, which form more stable complexes with ferric than ferrous iron.

All oxidation reactions for ferrous iron are exergonic and thus yield energy. The hypothesis has been put forward that these reactions may serve as a source of energy in microbial metabolism (66).

Certain groups of iron bacteria deposit ferric hydroxide from ferrous salt solutions and their metabolism appears to be linked with the



oxidation of ferrous iron to the ferric form. According to Thimann (67), however, the autotrophic mode of life of these organisms has never been proved conclusively.

A great many algae, especially the blue greens and the desmides, precipitate iron from ferruginous waters (26). However, there is no reason to believe that the oxidation and precipitation of iron are of importance in their metabolism. It appears to be well established, however, that the oxidation of the sulfide and polysulfide in ferrous sulfide and pyrite,  $\text{FeS}_2$ , can be mediated by thiobacteria.

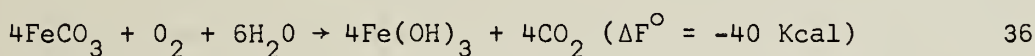
In the absence of dissolved oxygen, which may occur in eutrophic lakes during periods of stagnation, favorable conditions for the reduction of ferric iron to the ferrous form may prevail (68). Under these conditions ferrous iron may be soluble up to a few mg/l depending on the alkalinity and pH. Oborn and Hem (69) demonstrated in laboratory studies that an anaerobic condition can be developed in a system where aquatic vegetation and a microbial population are actively growing. This is always marked by a depletion of dissolved oxygen, a decrease in the redox potential and a reduction of ferric iron to the ferrous state.

There are various forms of autotrophic microbial life which are related to iron in one way or the other. For over 80 years, prior to the work of Cholodny (70), the twisted ribbons of ferric hydroxide found in iron bearing natural waters exposed to atmospheric oxygen were described as living organisms of the genera Gallionella and Spirophyllum. From the report of Pringsheim (71), it is now accepted that Gallionella and Spirophyllum are synonymous. The twisted stalks of these bacteria were later found to be non-living sheath material secreted by the actual organism. Presently, four forms of Gallionella ferruginea have been isolated from



natural sources. As suggested by Pringsheim, these may be the different morphological variations of the same species.

In an attempt to grow iron bacteria, Lieske (72) found that enrichment cultures did not grow unless some ferrous salts (usually carbonates) were added to the medium. He observed no growth in the absence of CO<sub>2</sub> or air, while there was definite growth aerobically in a purified mineral medium containing ferrous carbonate. He, therefore, concluded that the organism was autotrophic and synthesized cell carbon by reducing CO<sub>2</sub> obtained from the following reaction:



Growth could be inhibited by peptone, sucrose, or asparagine, much as in the case of nitrifiers.

Using iron filings and a purified mineral medium, Lieske (72) found 496 mg of bacteria were produced while 217 mg of Fe<sup>++</sup> were oxidized. Of the bacterial cell mass only 21 mg (about 4 percent) were organic matter. It was found that 3 mg of carbon were converted to organic matter. Starkey (73) indicated that oxidation of 217 mg of iron would only lead to 0.3 mg of cell material assuming a free energy efficiency of 8 percent. He concluded that the cultures developed by Lieske might have contained Nitrosomonas and that there were other possible sources of error. The evidence was therefore inconclusive. On several occasions, growth of Gallionella and deposition of iron have been observed under anaerobic conditions, though only in crude cultures (74). This certainly does not suggest obligate oxidative autotrophy.

Reporting on their growth studies, Kucera and Wolfe (75) remarked



that

"....initially a narrow zone is indicated in which it is possible to compete with auto-oxidation of ferrous iron. If an upward diffusion of ferrous ions and a downward diffusion of oxygen molecules is pictured, then it is possible for G. ferruginea to initiate growth only at a position where an adequate supply of both ferrous ions and oxygen are available...."

They also found growth to be maximum at 25°C with no growth above 30°C. This observation assists in explaining the abundance of this organism in water supplies and even in filters. Kucera and Wolfe were able to grow the organism in continuous subculture at 25°C. The colonies were "white and cottony" and the culture needed CO<sub>2</sub>, FeS and tap water besides other growth factors. Best growth was obtained at pH between 6.3 to 6.6. Wolfe (75) reported that the growth factor that was contributed by tap water was calcium. He confirmed that the organism was an autotroph and obtained its energy by oxidizing ferrous salts and its carbon from carbonates or carbon dioxide. It synthesized organic nitrogen from ammonium chloride. It can therefore exist in waters devoid of organic matter.

Another species of iron bacteria, Ferrobacter ferrooxidans, oxidizes ferrous iron to the ferric form vigorously at pH 3 to 3.6 and at a temperature of 37°C (76). The same bacteria also oxidizes free sulfur (77). A very similar organism, Thiobacillus ferrooxidans, isolated from coal mine drainage has been found to oxidize thiosulfates vigorously (78). This organism requires a high ratio of sulfate to chloride in order to oxidize iron and it cannot oxidize FeCl<sub>2</sub>. It is believed that these organisms are also true iron-oxidizing autotrophs. Still another kind of iron oxidizing bacteria has been successfully grown in a mineral medium containing ferrous ammonium citrate and at a pH of 6.0 (79). Complete morphology and the metabolic pattern of this species is, however, yet to be determined.



Thus far, the discussion on bacterial growth in a filter has been confined to iron bacteria. However, the reduction of ferric iron to the ferrous form may be related to the anaerobic condition that prevails in some filters occasionally when the dissolved oxygen is totally depleted due to the activity of aerobic bacteria.

Many plants treating water containing ammonia have encountered problems in carrying oxygen or chlorine through the filter. Nitrosomonas and Nitrobacter, which are quite abundant in nature, can oxidize ammonia to nitrite (Nitrosomonas) and nitrite to nitrate (Nitrobacter). Meyerhof (80) found by measuring oxidation rates that the optimum pH for the growth of Nitrosomonas was 8.5 to 8.8 and that for Nitrobacter it was about the same. However, at pH values of 6 and 9 (encountered frequently in natural waters) the oxidizing capacity of these organisms was 20 and 90 percent, respectively, of its maximum. There was a definite decrease in the nitrifying activity at pH values higher than 9.0. This may be due to the inability of the cells to use the  $\text{CO}_3^{=}$  ion as a source of  $\text{CO}_2$ , while they could use  $\text{HCO}_3^-$  (67). The activity of these organisms was also considerably reduced at pH values less than 5.0. However, most natural ground waters have a sufficient buffering capacity that it is unusual to encounter a water of such a low pH.

Since the nitrifiers are autotrophic, it is easy to see why their growth is not supported by organic matter. Actually, many organic compounds inhibit nitrification. Gelatin as well as many amines, alkaloids and even some amino acids inhibit nitrification (80). Guanidine and aniline derivatives were found to be potent inhibitors in soil enrichment cultures (81). Metal combining agents such as cyanide, thiourea (82), and especially allylthiourea (83) also inhibit nitrification. It appears that the inhibition



is due either to an interference with the metal-enzyme oxidase system (cyanide) or to a chemical relationship with the substrate ammonia (organic bases). Antibiotics do not seem to have any effect on Nitrosomonas as demonstrated by Lees who attempted to inhibit growth with streptomycin (84). However, Nitrobacter can be effectively inhibited by antibiotics (82).

In a natural water the depletion of dissolved oxygen may occur due to the bacterial oxidation of reducing gases, e.g.,  $\text{NH}_3$ ,  $\text{H}_2\text{S}$ ,  $\text{CH}_4$  (85). Equations 1 through 6 in Table 3 are a few examples of oxygen depleting reactions that may be encountered in a natural system. It can be seen from Equation 3 that complete nitrification of 2 mg/l of  $\text{NH}_4^+$ -nitrogen would consume the total amount of oxygen in an oxygen-saturated water.

In the coastal regions of Netherlands, the presence of high amounts of ammonia in ground waters is a common occurrence. Kooijmans (86) reported

"....if relatively high amounts of ammonia are present in the water this may result in anaerobic conditions in the lower part of the filter and troubles in iron and manganese removal. Redissolution of iron deposits in the filter bed may take place.....Nitrification is not a direct oxidation by the oxygen from the air, but it is a microbial process. Ammonia is first oxidized to nitrite by the activities of bacteria of genus Nitrosomonas and the nitrite is converted to nitrate by bacteria of the genus Nitrobacter. It will take some time, several weeks or months, before complete nitrification is achieved in a new filter. The nitrifying organisms develop relatively slowly and a certain equilibrium has to be established. The adverse effect of high ammonia content will consequently become perceptible only when the filters have been in operation for some time....."

In 1935, Feben (87) reported the problems with nitrification at a water treatment plant in Detroit, Michigan. The nitrifying bacteria, a Nitrococci in this case, could resist a dosage of chlorine as high as 7 mg/l. It was also observed that the nitrite formed had a chlorine demand of about 5 parts per part of nitrite nitrogen. This figure is in accord with



TABLE 3

## CHEMICAL CHANGES DUE TO NITRIFICATION

No.	Equation	Oxidant demand, mg/mg	$\Delta F^0$ , Kcal/mol	$E^0$ , volt,	Acidity ( $H^+$ ion), mol/mol	$HCO_3^-$ reduction ( $H^+ + HCO_3^- = H_2O + CO_2$ ), mol/mol
<u><math>O_2</math> demand</u>						
1	$NH_4^+ + 1.5O_2 = NO_2^- + 2H^+ + H_2O$	O:N=3.42	-45.94	--	H:N=2	$HCO_3^-$ :H = 1
2	$2NO_2^- + O_2 = 2NO_3^-$	O:N=1.13	-36.36	--	--	--
3	$NH_4^+ + 2O_2 = NO_3^- + 2H^+ + H_2O$	O:N=4.55	-64.12	--	H:N=2	$HCO_3^-$ :H = 1
4	$CH_4 + 2O_2 = 2H_2O + CO_2$	O:CH <sub>4</sub> =4.00	-193.60	--	H:C=2	$HCO_3^-$ :H = 1
5	$H_2S + 0.5O_2 = H_2O + S$	O:H <sub>2</sub> S=0.47	-41.50	--	--	--
6	$S + 1.5O_2 + H_2O = 2H^+ + SO_4^{2-}$	O:S=1.5	-118.00	--	H:S=2	$HCO_3^-$ :H = 1
<u><math>Cl_2</math> demand</u>						
7	$NH_3 + 3Cl_2 = NCl_3 + 3H^+ + 3Cl^-$	N:Cl <sub>2</sub> =15.3	NA	--	--	--
8	$NO_2^- + Cl_2 + H_2O = NO_3^- + 2H^+ + 2Cl^-$	N:Cl <sub>2</sub> =5.08	-25.84	--	--	--



TABLE 3 (cont.)

## CHEMICAL CHANGES DUE TO NITRIFICATION

No.	Equation	Oxidant demand, mg/mg	$\Delta F^0$ , Kcal/mol	$E^0$ , volt	Acidity ( $H^+$ ion), mol/mol	$HCO_3^-$ reduction ( $H^+ + HCO_3^- = H_2O + CO_2$ ), mol/mol
<u>Oxidation-Reduction Half Reactions</u>						
<u><math>O_2</math> as oxidizing agent</u>						
9a	$NH_4^+ + 2H_2O = NO_2^- + 8H^+ + 6e^-$	--	124.13	0.90		
9b	$1.5O_2 + 6H^+ + 6e^- = 3H_2O$	--	-170.07	-0.99		
10a	$2Fe^{+2} + 6H_2O = 2Fe(OH)_3 + 6H^+ + 2e^-$		48.00	1.04		
10b	$1/2 O_2 + 2e^- = O^{=}$		-60.10	-1.31		
11a	$NO_2^- + H_2O = NO_3^- + 2H^+ + 2e^-$	--	38.51	0.84		
11b	$0.5O_2 + 2H^+ + 2e^- = H_2O$	--	-56.69	-1.23		
<u><math>Fe^{+3}</math> as oxidizing agent</u>						
12a	$NO_2^- + H_2O = NO_3^- + 2H^+ + 2e^-$		38.51	0.84		
12b	$2Fe^{+3} + 2e^- = 2Fe^{+2}$	$Fe^{+3}; N=7.95$	-35.54	-0.77		



TABLE 3 (cont.)

## CHEMICAL CHANGES DUE TO NITRIFICATION

No.	Equation	Oxidant demand, mg/mg	$\Delta F^0$ , Kcal/mol	$E^0$ , volt	Acidity ( $H^+$ ion), mol/mol	$HCO_3^-$ reduction ( $H^+ + HCO_3^- = H_2O + CO_2$ ), mol/mol
<u><math>Cl_2</math> as oxidizing agent</u>						
13a	$2Fe^{+2} + 6H_2O = 2Fe(OH)_3 + 6H^+ + 2e^-$		48.00	1.04		
13b	$Cl_2 + 2e^- = 2Cl^-$	$Cl_2:Fe^{+2}=0.64$	-64.35	-1.40		
14a	$NO_2^- + H_2O = NO_3^- + 2H^+ + 2e^-$		38.51	0.84		
14b	$Cl_2 + 2e^- = 2Cl^-$	--	-64.35	-1.40		



Equation 6 of Table 3. Larson (88) reported that nitrification was one of the major causes of oxygen depletion and consequent reduction of ferric iron to the ferrous form observed at the treatment plant at the University of Illinois. He also indicated that as nitrification of ammonia results in production of acid, it promoted dissolution of iron deposits in the distribution system. Furthermore, a slight decrease in alkalinity was observed as a result of nitrification. Hill (89) reported a pH drop from 8.5 to 6.3 and a decrease in alkalinity from 134 to 17 as a result of nitrification.

Non-submerged filtration has been successfully employed in Netherlands to treat ground waters with a high concentration of iron, manganese and ammonia (23)(90). The sequence of successive oxidation phases and oxidation-reduction potentials in such a system is: iron, ammonia and manganese oxidation. Complete removal of the three components could be achieved by a single filtration in non-submerged filters by simultaneous passage of air and water. Buswell (85) suggested the use of phosphates to precipitate ammonia as calcium and magnesium ammonium phosphates prior to filtration. In France, reportedly, 7 mg/l of ammonia could be removed by a contact bed filter prior to rapid sand filtration (86). Compressed air was first injected into the water that passed upward through a contact bed. In the course of time an abundant growth of nitrifying organisms was developed that reduced the ammonia content to a very low level. Backwashing of the contact filter was not necessary, as the upward flow circulation prevented excessive deposits on the contact material.



### 3. MATERIALS AND METHODS

#### 3.1 Objectives of the Study

In Illinois, and probably throughout the world, the most common method of removing iron from ground waters is by aeration, followed by a reaction or settling period and sand filtration. In evaluating the efficiency of a number of iron removal plants in Illinois, it was observed that, in almost every plant investigated, a marked decrease in dissolved oxygen occurred in the filters (24). This observation was often associated with a high iron content in the filtered water. Consequently, a field study was initiated at one of these plants, namely, Clinton, Illinois, to determine filter performance in the removal of iron.

The treatment plant at Clinton, Illinois, had experienced difficulties with iron removal for quite some time. It was believed that the accumulation of a bacterial slime in the filters might be associated with the poor iron removal. The plant treats water obtained from several drilled wells. The unit processes employed are aeration by coke tray aerators, detention (60 minutes or less) filtration and ion exchange. Figure 5 shows a schematic diagram of the treatment plant at Clinton.

The general raw water characteristics at Clinton are shown in Table 4. The observed total iron concentration of the filtered water fell, most of the time, within the range of 0.3 to 0.6 mg/l. However, it was observed to be as high as 1.2 mg/l on one occasion. A considerable fraction of the iron passing through the filter was ferrous in form. In recent years, a considerable slime growth had been observed on the anthracite filter medium. A copper sulfate dosage of 1.0 mg/l prior to filtration was used for a period of time to control the biological growth in the filter. This



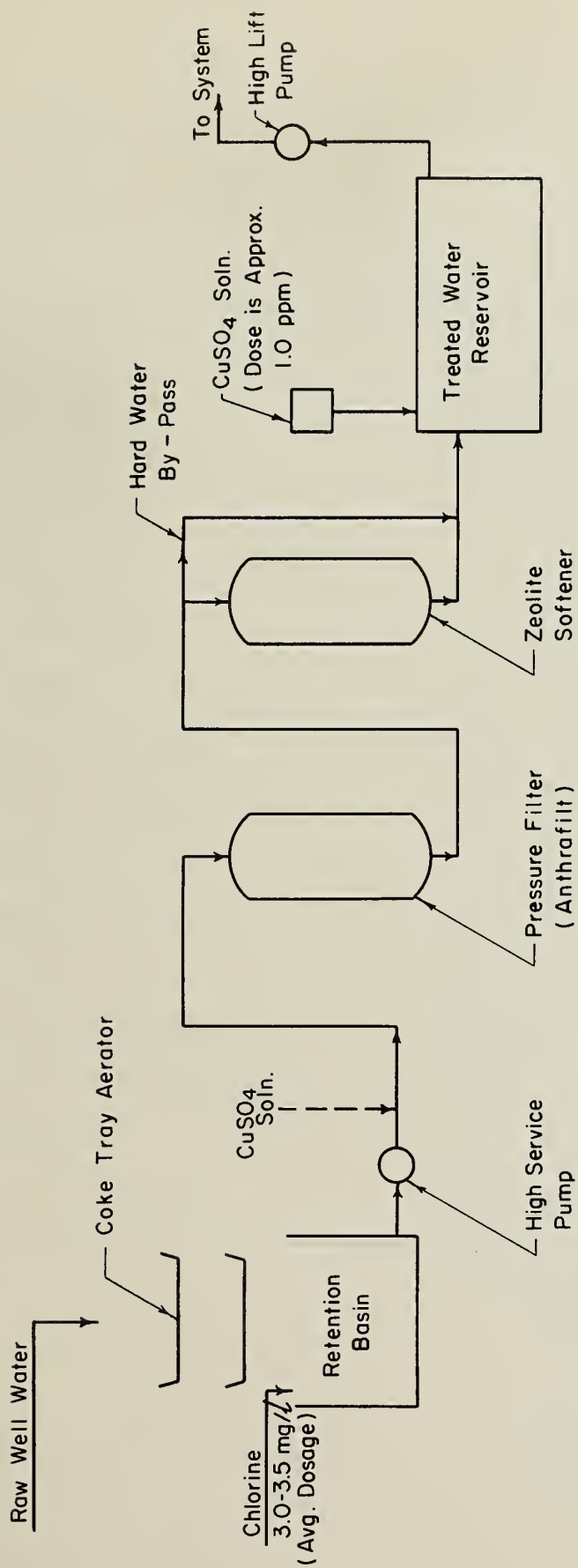


FIG. 5. SCHEMATIC FLOW DIAGRAM OF THE WATER TREATMENT PLANT  
AT CLINTON, ILLINOIS



TABLE 4

## AVERAGE RAW WATER CHARACTERISTICS AT CLINTON, ILLINOIS

---

Total Iron	2.2 - 3.1 mg/l
Ferrous Iron	1.6 - 2.0 mg/l
pH	7.1 - 7.3
Alkalinity	430 - 450 mg/l as $\text{CaCO}_3$
Total Hardness	325 - 340 mg/l as $\text{CaCO}_3$
Calcium	70 - 72 mg/l
Dissolved Oxygen	nil
Chemical Oxygen Demand	30 - 35 mg/l
Organic Nitrogen	2.0 - 3.0 mg/l
Ammonia Nitrogen	2.7 - 3.2 mg/l
Nitrite Nitrogen	nil
Nitrate Nitrogen	nil
Total Dissolved Solids	518 mg/l
Chloride	52 - 56 mg/l
Redox Potential	+320 to +340 m.volts

---



resulted in the passage of still higher quantities of iron by the filters due, it was believed, to the dispersion of the ferric iron precipitate by copper within the filters. The plant is still using copper sulfate but the point of application follows filtration so as to control slime growth in the distribution system.

The study to be reported herein was designed to investigate the removal of iron by sand filtration. In particular, the role of the biological growth that often occurs in a rapid sand filter, and the influence of chemical conditions in a filter on the removal of iron were investigated. A pilot plant was used for this study.

Experiments were designed to determine the performance of a new filter in relation to the depth of penetration of iron floc, the concentration of dissolved oxygen at any depth, the head loss and the pattern of breakthrough of iron through the filters.

Preliminary studies prior to the present investigation indicated a gradual deterioration of water quality in some plants as the filters became "ripened" or after a biological growth has developed. Investigations were carried out on "ripened" pilot plant filters to determine the extent of biological growth, loss of dissolved oxygen and the concentration and forms of iron being passed at various filter depths during a filtration period of 24-48 hours. The occurrence of reducing conditions in an operating filter as well as the passage of iron could, therefore, be observed.

Since the water at Clinton contained considerable amounts of ammonia, experiments were designed to investigate the possibility of nitrification which might account for the marked depletion of dissolved oxygen within the filter.



In order to determine whether the biological growth, the nitrifying organisms in particular, were responsible for the loss of D.O. and the reduction of iron from the ferric to the ferrous form, inhibitors, e.g., thiourea and "Roccal,"\* were used to control the growth of Nitrosomonas (nitrite formers) and all other bacterial growths respectively. An improvement of the filter performance in removing iron under such conditions would therefore confirm the role of bacteria in the deterioration of an iron removal filter.

Prechlorination was used on a new and "ripened" filter in an effort to determine whether the maintenance of a chlorine residual through the filters would control the growth of bacteria. In addition, information of the amount of chlorine required to maintain a residual could be obtained.

In short, this report centers around an investigation of the causative agents for the reducing conditions that develop in a "ripened" filter and the remedial measures that can be employed to alleviate such problems.

### 3.2 Design and Description of Equipment

A continuous flow pilot plant was designed as an integrated series of unit processes. This approach provided flexibility in operation and allowed experiments to be made under controlled conditions.

Rubber, glass and transparent rigid plastics ("Lucite" and "Plexiglas") were used to construct the apparatus so as to guard against any

---

\*Roccal (10 percent solution) - A product of Winthrop Laboratories, New York.  
 Active ingredients - Alkyldimethylbenzylammonium chloride ( $C_{12}$ ,  $C_{14}$ ,  $C_{16}$  and other related alkyl groups from  $C_8$  to  $C_{18}$ ) - 10 percent.  
 Inert ingredient - Water - 90 percent.



contact between water and iron. The entire apparatus was made so that it could be easily disassembled and transported for field studies.

The unit processes considered for the design were:

- a. constant-head flow regulator
- b. aerator
- c. reaction-sedimentation basin
- d. rapid sand filter; a bank of four filters with different depths of filtering medium.

Figure 6 is a schematic flow diagram of the assembled pilot plant. Stands, supports and accessories were used to obtain gravity flow through the plant from the overflow stand pipe. Pumping was necessary only for chemicals that were added directly to the reaction-sedimentation tank or to the filters. The well pump at Clinton was used to supply raw water to the overflow stand pipe.

All components of the pilot plant were designed to enable operation of four filters at a rate of 2 gpm/sq ft. A description of the components making up the pilot plant is given below.

Aerator: The aerator was a multiple pass, diffused air unit with the water introduced under gravity pressure. The raw water was aerated using compressed air, dispersed through a coarse carborundum diffuser. The diffuser consisted of a hollow carborundum cylinder, 3 inches high, 2-inch o.d. and 0.5 inches thick. With a water flow of 1.48 liters/minute required to supply the four filters at 2 gpm/sq ft, the detention time in the aerator, as determined by a tracer study, was 3.25 minutes. The air rate was so adjusted as to impart a dissolved oxygen concentration of 6.5 to 8.0 mg/l to the raw water. The volume of the aerator was 6.0 liters. The water flowed via an overflow weir into the reaction-sedimentation tank.



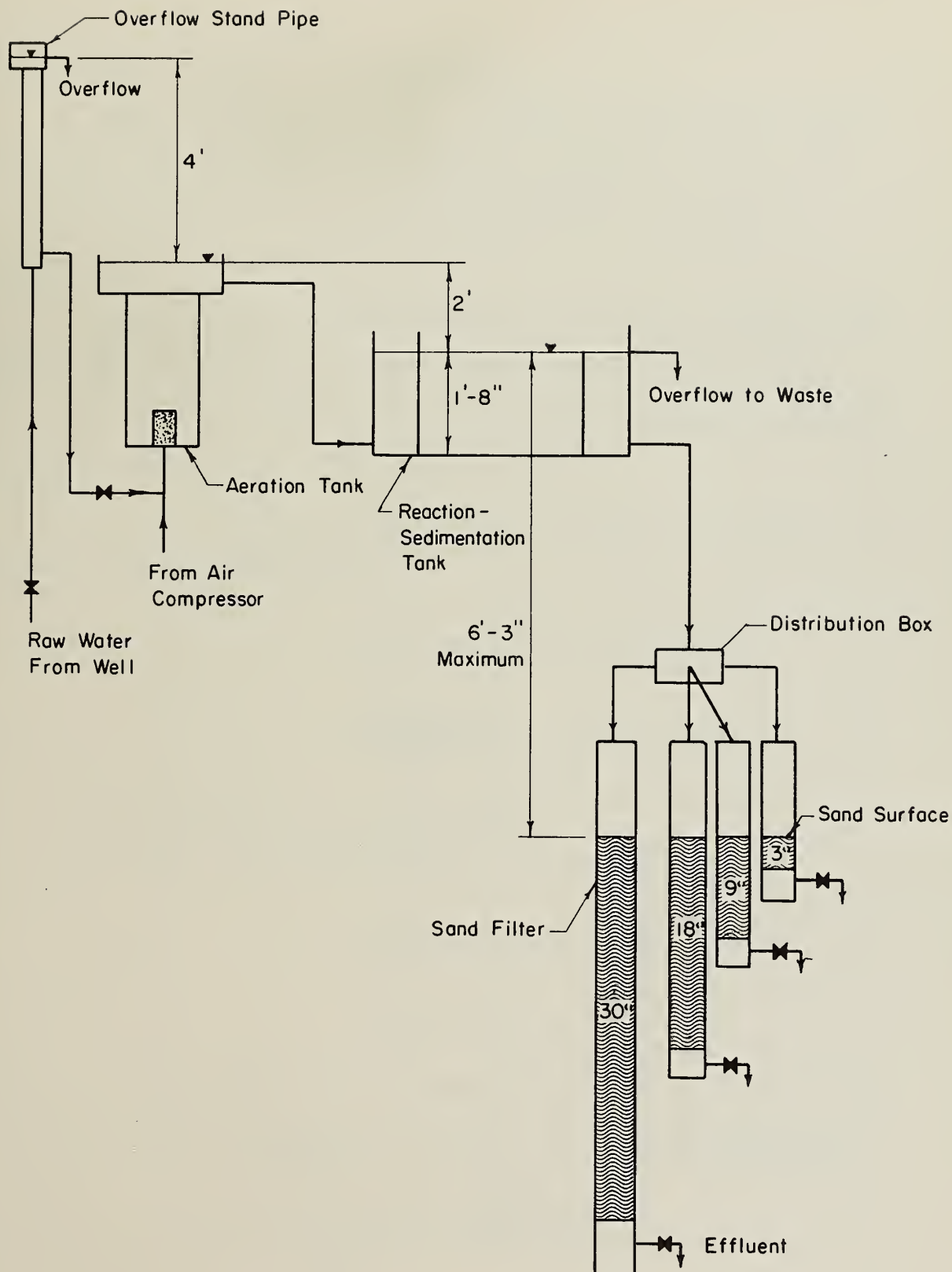


FIG. 6. SCHEMATIC FLOW DIAGRAM OF PILOT PLANT



Figure 7 shows the details of the aerator.

Reaction-Sedimentation Tank: The tank for the combined purpose of providing time for completing the chemical oxidation of ferrous iron and for sedimentation of insoluble iron precipitate was designed as described below.

A reaction tank providing 60 minutes detention is normally provided for the precipitation of iron following aeration of raw waters in central Illinois (44). The detention time chosen for design was therefore 60 minutes.

The flow required to supply the four filters at a rate of 2 gpm/sq ft was calculated to be,

$$4 \times \pi/4 \times (3/12)^2 \times 2 = 0.3936 \text{ gpm}$$

$$= \frac{0.3936 \times 8.34}{62.4} = 0.0526 \text{ cu ft/min}$$

Design detention time = 60 minutes.

Therefore, the required volume of the tank was,

$$0.0526 \text{ cu ft/min} \times 60 \text{ min}$$

$$= 3.156 \text{ cu ft.}$$

Adopting a surface loading rate of 400 gpd/sq ft for design as recommended per the "Ten State Standards,"\* the surface area =  $\frac{\text{Flow rate}}{\text{Surface loading rate}}$

or

$$A_s = \frac{Q}{V} = \frac{0.0526}{400} \frac{\text{cfm}}{\text{gpd/ft}^2}$$

$$= \frac{0.0526}{0.036} \frac{\text{cfm}}{\text{cfm/ft}^2}$$

\*Recommended Standards for Water Works, Bull. 42, New York State Health Dept., May, 1962.



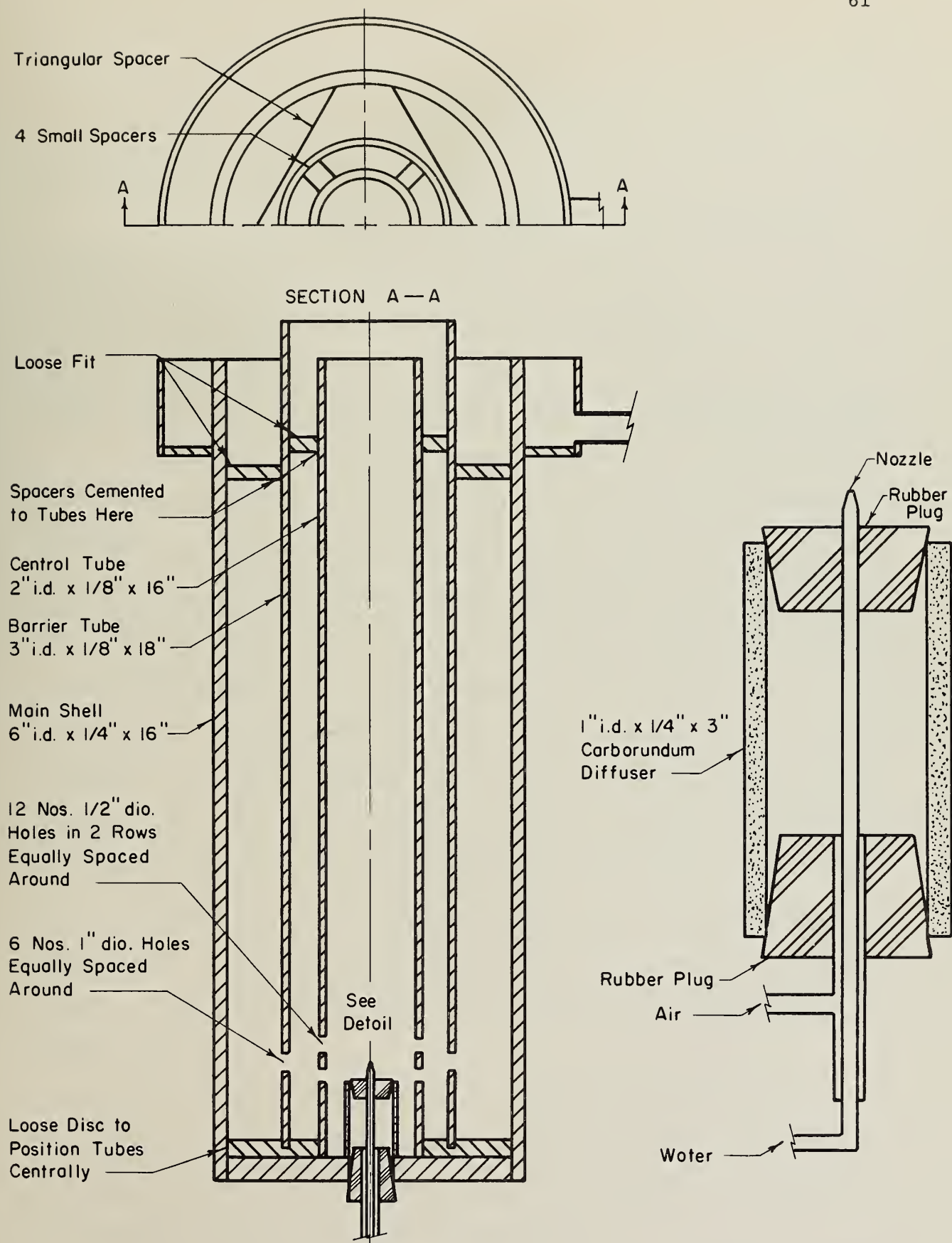


FIG. 7. AERATION DEVICE



$$= 1.42 \text{ ft}^2$$

The dimensions of the tank chosen were

$$= 2 \text{ ft (length)} \times 1 \text{ ft (width)} \times 1.67 \text{ ft (water depth)}$$

Therefore, surface area provided = 2 sq ft > 1.42 sq ft

volume provided = 3.32 cu ft > 3.156 cu ft

tank capacity = 25 gals.

Actual height of the tank was 2 feet which provided a freeboard of 4 inches.

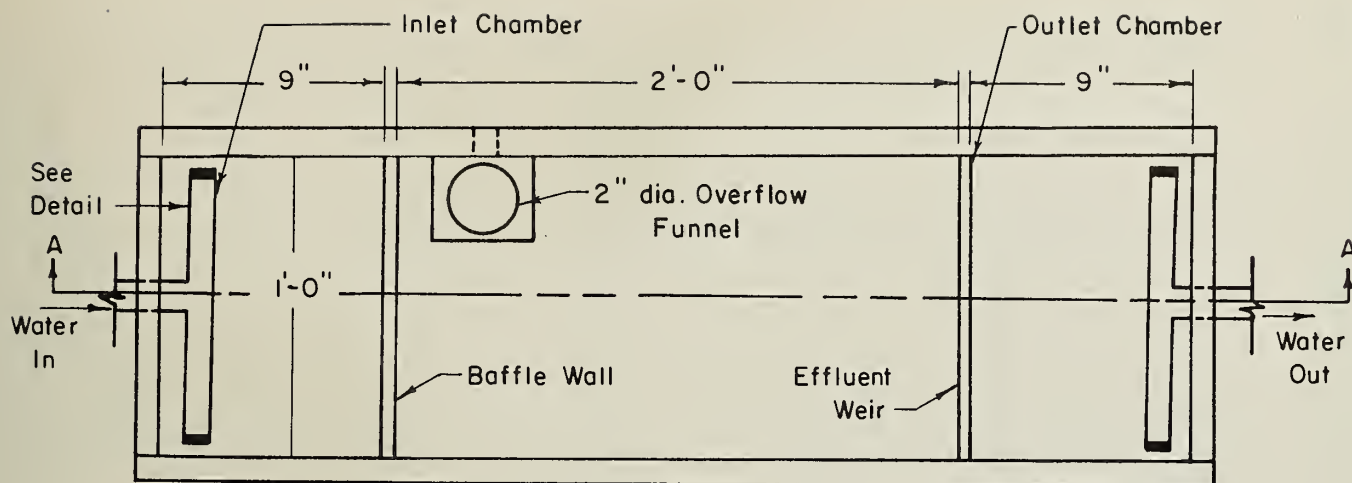
A plastic inlet device introduced the water at a point 2 inches from the bottom and at one end of the tank. The inlet device consisted of a 1-inch i.d., 9-inch-long tube having 1/8-inch diameter holes 2-inch o.c. which directed the water downward, and simultaneously distributed it over the full width of the inlet chamber. For uniform and non-turbulent distribution of the influent water an inlet chamber of size 0.75 ft x 1 ft x 1.67 ft was provided. This was partitioned from the main reaction tank by a baffle wall which had 1/2-inch diameter holes located horizontally and vertically 3 inches apart. The outlet chamber was similar to the inlet chamber except that the wall separating it from the main tank had no holes in it. Therefore, the entire length of the dividing wall, 1 foot, served as a free falling weir. The outlet device was similar to the inlet device in every respect. Figure 8 shows the detail of the reaction tank with the inlet and outlet devices.

The actual detention time was determined using a methylene blue dye. Figure 9 shows a plot of percent transmittance of the effluent from the tank at various times after the introduction of the dye. The actual mean detention time was found to be 48 minutes.

Filters and Appurtenances: From the reaction-sedimentation tank



## PLAN



## SECTION A-A

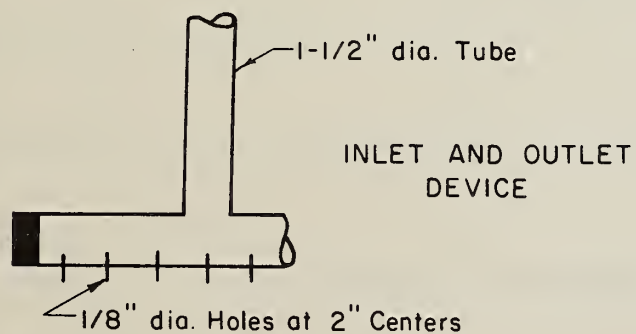
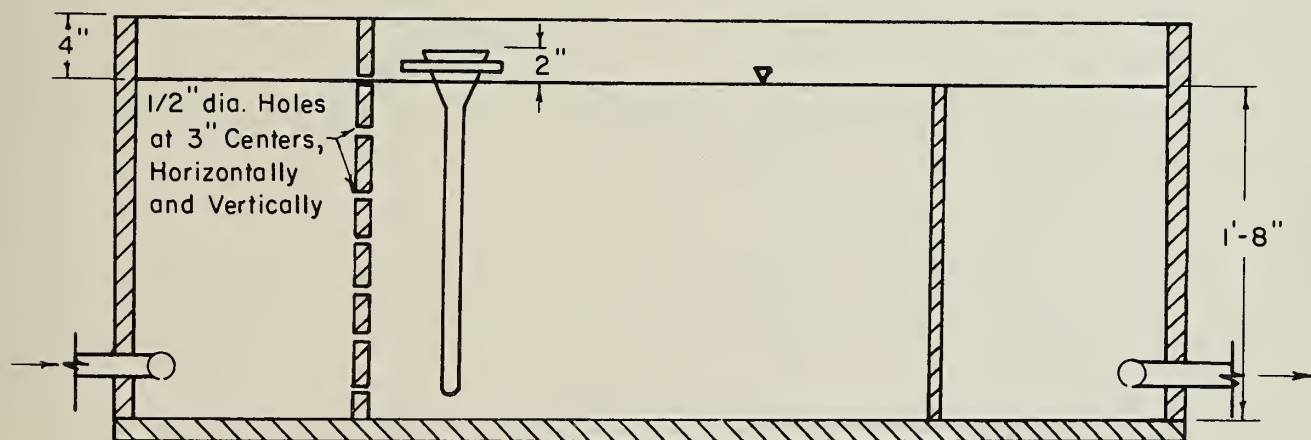


FIG. 8. REACTION-SEDIMENTATION TANK



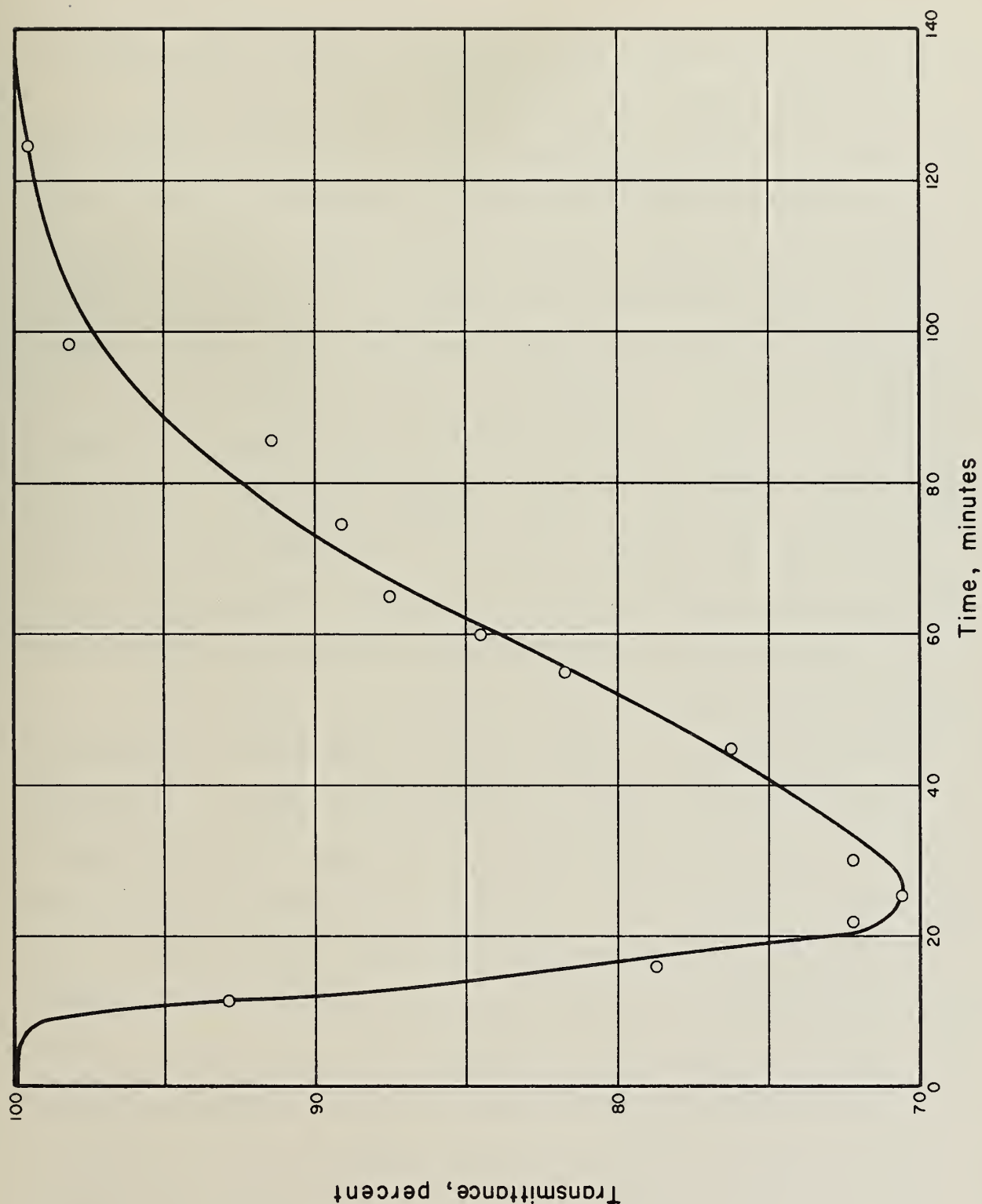


FIG. 9. STUDY FOR FLOWTHROUGH TIME IN THE REACTION-SEDIMENTATION TANK

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 Civil Engineering Department  
 B106 C. E. Building  
 University of Illinois  
 Urbana, Illinois 61801



the water flowed through a distribution chamber and then to the filters.

In an earlier pilot plant study of iron removal problems were encountered in collecting representative samples at different depths of a sand filter (17). Therefore, in order to facilitate the collection of samples at different depths without disturbing the hydraulic conditions, a bank of four filters was designed with varying depths of sand: 3, 9, 18 and 30 inches. This arrangement permitted the degree of iron removal, the extent of biological growth, and the physical conditions at different levels of a conventional rapid sand filter to be determined. The filters were made of 3-inch i.d. "Plexiglas" tubes, 1/4 inch thick. This diameter provided a sand surface area of 0.05 sq ft. Figure 10 shows the details of the 30-inch filter. The other filters were similar to the 30-inch filter in every respect except for the depth of the filtering medium.

The underdrain system for each filter was graded gravel passing 1/4-inch mesh and retained on a 1/8-inch mesh. The gravel layer had a depth of 4, 4, 6 and 8 inches for the 3-, 9-, 18- and 30-inch filters respectively and was supported on a perforated "Lucite" disc. The sand, in turn, was separated from the gravel by a similar perforated Lucite disc. Below the gravel layer a depth of 4 inches was provided to serve as the clear well. Two 5/16-inch i.d. "Lucite" tubes were cemented onto the filter tubes in diametrically opposite positions on each clear well. One of these tubes was connected to a mercury manometer while the other was used as a combination effluent sampling and backwash connection. Filter influent water entered approximately 20 inches above the sand surface in all four filters. Backwash water flowed out through a 3/8-inch plastic pipe connection in the top flange of each filter. On the 30-inch filter, 1/2-inch-diameter holes were provided at sand depths of 1/4, 3, 9, 18 and 28 inches



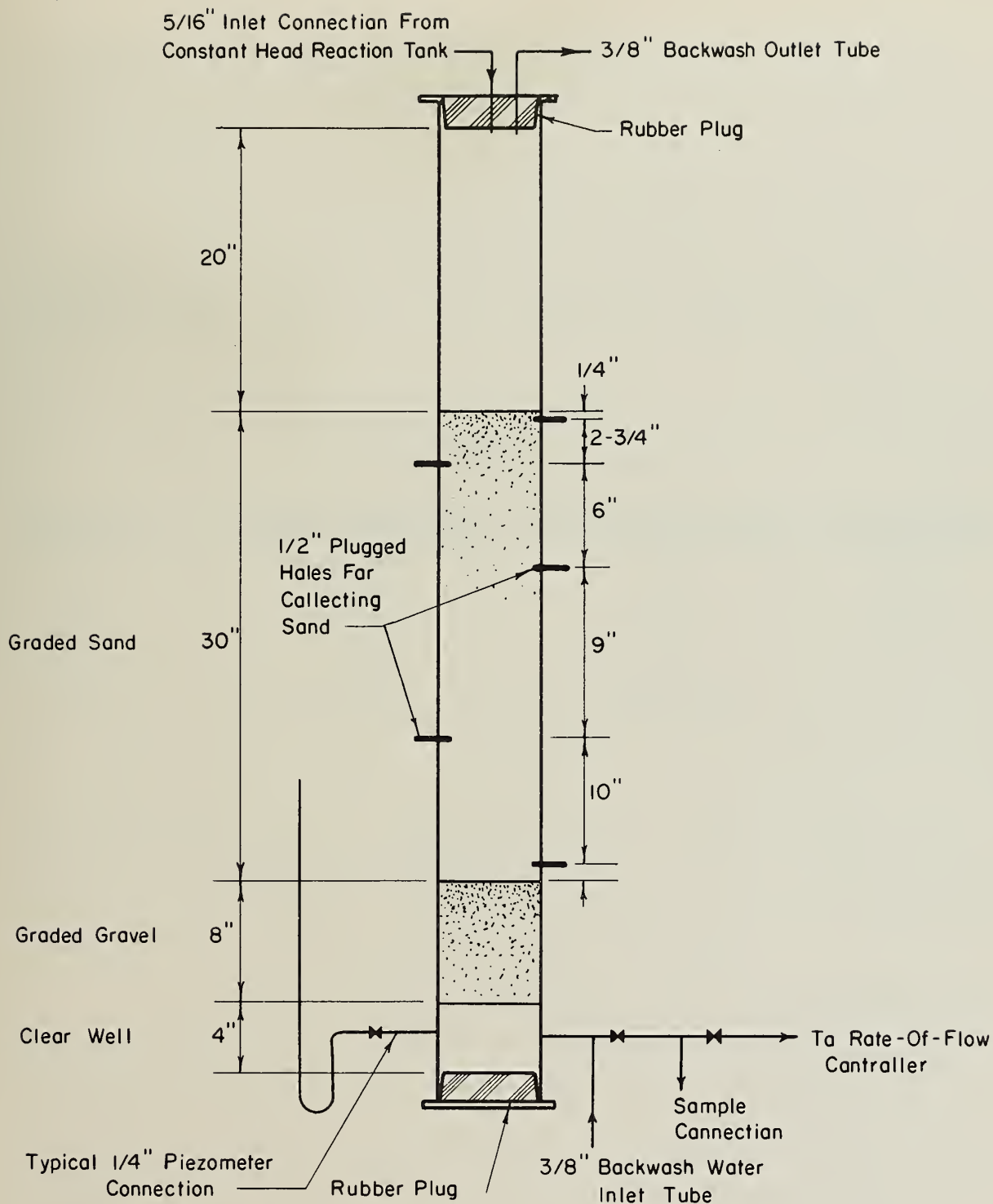


FIG. 10. SAND FILTER DETAILS



to enable collection of sand samples. These holes were arranged in an alternating fashion to prevent two adjacent holes from lying directly in a vertical line.

Filter sand was obtained from the Norther Gravel Company of Muscatine, Iowa. The sand was analyzed for size distribution using U.S. Standard Sieves. The results of the analysis are shown in Table 5. A

TABLE 5  
SIEVE ANALYSIS FOR FILTER SAND

Sieve No.	Normal Opening (mm)	Wt. Retained (gm)	Percent Fine
16	1.190	0.63	99.37
20	0.840	3.67	95.70
30	0.590	78.33	17.37
50	0.297	16.67	0.70
60	0.250	0.83	0
70	0.210	Negligible	0

plot of "percent fine" vs. "logarithm of size" is shown in Figure 11 on normal probability paper. The effective diameter and the uniformity coefficient of this sand were 0.51 mm and 1.40 respectively.

The effluent from each filter passed into a float operated rate of flow controller shown in Figure 12. The controller maintained a constant rate of filtration of 2 gpm/sq ft by holding a constant head on a 1/2-inch needle valve. The float mechanism consisted of a 4-inch-diameter copper float with a 3/4-inch inlet valve. Each float chamber was made of 3/8-inch-thick "Lucite" and had a size of 9 inches x 9 inches x 15 inches.

As the head loss through the filter increased during a filtration period the float valve would gradually open to maintain a constant rate of filtration and, consequently, the head on the needle valve would decrease



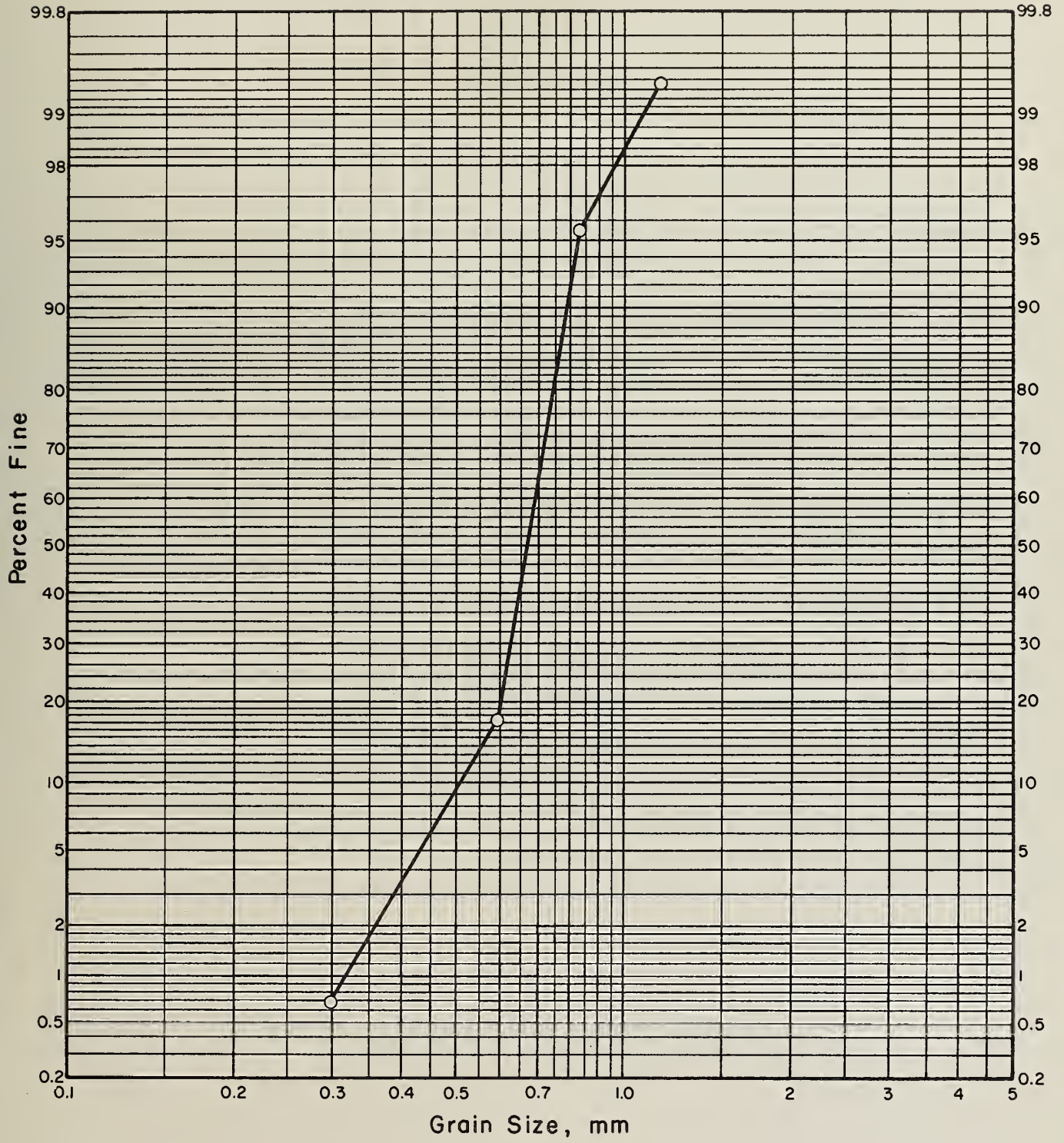


FIG. II. GRAIN SIZE DISTRIBUTION



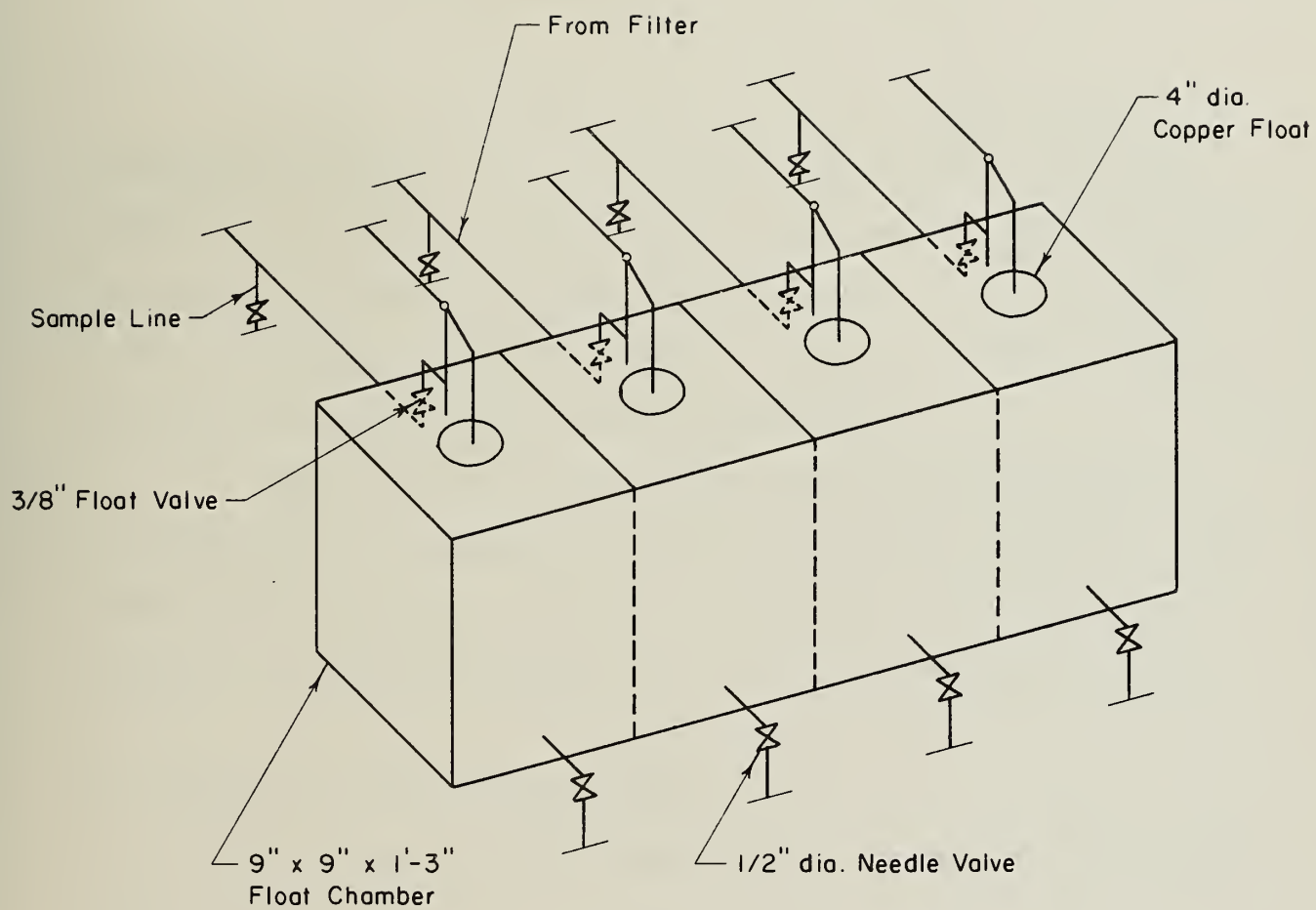


FIG. 12. RATE-OF-FLOW CONTROL DEVICE



slightly. This resulted in a slight decrease in the rate of filtration approximately in proportion to  $\sqrt{\Delta h}$  ( $\Delta h$  = head change). In order to maintain constant rate, the needle valve was opened slightly to compensate for the change in head.

The float valves functioned fairly well. However, problems were encountered occasionally due to bacterial and algal growth in the float chambers which clogged the needle valves. Copper sulfate solution was used to control such growth during the filtration period. In spite of this preventive measure, some growth occurred. Therefore, the float chambers were cleaned when the filters were being backwashed.

Feeding of chlorine and inhibitor solutions for controlling bacterial growth was accomplished by means of a positive displacement pump (Sigma pump manufactured by Schaar & Co., Chicago, Illinois) which had a capacity of delivering a maximum flow of 8.5 liters per hour at 0 p.s.i.

### 3.3 Analytical Methods and Techniques

The following analyses were performed to characterize the water at any stage of treatment.

- a) Alkalinity
- b) Bacterial count
- c) Chloride
- d) Residual chlorine
- e) Chemical oxygen demand (COD)
- f) Total hardness
- g) Calcium hardness
- h) Total iron
- i) Ferrous iron



- j) Dissolved oxygen
- k) Ammonia nitrogen
- l) Organic nitrogen
- m) Nitrite nitrogen
- n) Nitrate nitrogen
- o) pH measurement
- p) Oxidation-reduction potential
- q) Total dissolved solids
- r) Temperature

With the exception of the determinations detailed in the following discussion, all analytical tests were performed according to the procedures given in Standard Methods, 11th Edition (91).

#### 3.3.1 Chemical Oxygen Demand

The method used for the determination of COD was a modification of the procedure outlined in Standard Methods. Mercuric sulfate (0.4 gm) was placed in the refluxing flask. A 20-ml water sample or an aliquot diluted to 20 ml with distilled water was then added to the flask and mixed. This was followed by the addition of 10 ml of standard potassium dichromate solution (0.25 N) and 30 ml of conc.  $\text{H}_2\text{SO}_4$  containing  $\text{Ag}_2\text{SO}_4$  (22 g of  $\text{Ag}_2\text{SO}_4$  per 9-pound bottle of conc.  $\text{H}_2\text{SO}_4$ ) in that order. The contents of the flask were mixed and refluxed for 2 hours. The excess dichromate was then titrated with 0.10 N ferrous ammonium sulfate solution, using ferroin indicator.

#### 3.3.2 Total Hardness and Calcium

These determinations were made in the same manner as outlined



in Standard Methods but using the Hach Chemical Company compounds, "Univer I" as the indicator for the total hardness and "Cal-Ver II" as the indicator in the calcium determination. "Titra-Ver" (EDTA), another product of Hach Chemical Co., was used as titrant in both determinations.

### 3.3.3 Iron Determination

#### a) Ferrous Iron

Considerable uncertainty exists in the analytical determination of ferrous iron in the presence of ferric iron. The method used for the present work was a modification of the method suggested by Lee and Stumm (92). This was found necessary as it was demonstrated by the author that in highly alkaline waters ferrous iron can exist in solution as well as in the insoluble form (basic carbonates,  $\text{FeCO}_3 \cdot \text{Fe(OH)}_2$ ) even in the presence of oxygen (93). Ferrous iron may also be adsorbed on ferric oxide hydrates. Therefore, two different analyses were made for ferrous iron, namely, soluble ferrous and total ferrous (soluble and insoluble or adsorbed ferrous) iron.

#### i) Total ferrous iron

a) A 5- to 10-ml sample was pipetted into a 125-ml separatory funnel containing 0.5 ml conc. HCl with mixing.

b) Ten ml of pH 4.0 buffer (sodium acetate plus acetic acid) were then added to the separatory funnel, again, with mixing.

c) Fifteen ml of 0.001 M 4,7-diphenyl-1,10 phenanthroline (Batho-phenanthroline) were added to the separatory funnel and contents of the funnel were mixed once more. Fifteen minutes were allowed for color development.

d) The colored phase was extracted with 10 ml of iso amyl alcohol



and made up to 50 ml with 100 percent ethyl alcohol.

e) The total ferrous iron content was determined colorimetrically using a model DU spectrophotometer manufactured by Beckman Instruments, Inc.

ii) Soluble ferrous iron.

The determination of soluble ferrous iron was identical to that of total ferrous iron. However, this determination was made on the filtrate obtained by filtering a 5- to 10-ml sample through a 0.45  $\mu$  membrane filter.

### 3.3.4 Oxidation-Reduction Potential Measurement

The ORP measurements were made with a Model G pH meter manufactured by Beckman Instruments, Inc. The meter was standardized with a saturated quinhydrone solution buffered to pH 4.0. This solution was prepared by adding 1 g of reagent grade quinhydrone powder to 5 ml of 1 M pH 4.0 biphthalate buffer. The Nernst equation for quinone-hydroquinone couple is given by:

$$E_{\text{O}}(\text{volts}) = 0.6994 - 0.000198 (T) \text{ pH} \quad 38$$

where, T = Temperature (Absolute).

At  $T = 25^{\circ} \text{C} = 298^{\circ} \text{Abs.}$  and  $\text{pH} = 4$

$$E_{\text{O}} = 0.464 \text{ volts.}$$

Since the measurement was made using a platinum and calomel electrode pair, and as the saturated KCl (calomel electrode) had an  $E_{\text{O}}$  value of 0.246 volt, the  $E_{\text{O}}$  of quinhydrone indicated by the meter in such a system was

$$E_{\text{O}} = 0.464 - 0.246 = 0.218 \text{ volt.}$$

(Q-H<sub>2</sub>Q)



Any deviation from this value was regarded as instrumental error and was added algebraically to the observed ORP value of a measured sample. If the reference electrode voltage,  $E_{\text{ref}}$  (the voltage of the calomel-platinum electrode pair in quinhydrone solution) be 0.235 volts, then the instrumental error would be,

$$0.218 - 0.235 = - 0.17 \text{ volt.}$$

$E_h$  values can be calculated from measured ORP values using the following relationship.

$$E_h = E_{\text{obs.}} + E_{\text{ref.}}$$

For example, let the  $E_{\text{obs.}}$  value for a sample be 0.10 volt.

$$\begin{aligned} \text{Therefore, } E_h &= 0.100 + (0.246 - 0.17) \\ &= +0.329 \text{ volt.} \end{aligned}$$

The ORP measurements were made in a flowing cell through which the water sample was passed during measurements.

The other analytical measurements are listed in Table 6.

### 3.4 Operation of the Pilot Plant

The data in this study were collected for the most part during the summer months, May through September, of 1963, 1964 and 1965. The pilot plant was set at the pump house for well No. 6 at Clinton, Illinois. The raw water used for the entire study was obtained from well No. 6.

During the first eight weeks of operation each summer, the pilot plant operated satisfactorily and produced water of acceptable quality. The investigations during this period were comprised mostly of head loss studies and routine measurements of iron, pH, alkalinity, DO, standard

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University of Illinois  
B106 NCEL  
208 N. Romine Street  
Urbana, Illinois 61801



TABLE 6  
SUMMARY OF ANALYTICAL METHODS

Determination	Std. Methods 11th Ed.	Method Used	Comment
Alkalinity	Yes	Amperimetric Titration	
Chloride	Yes	Colorimetric Titration	Mercuric nitrate method
Total iron	Yes	Spectro- photometric	
Dissolved Oxygen	Yes	Colorimetric Titration	Azide modification of Winkler method
Ammonia Nitrogen	Yes	Kjeldahl	Distillate collected in $H_3BO_4$ . Direct nesslerization used for later work.
Organic Nitrogen	Yes	-do-	
Nitrite Nitrogen	Yes	Colorimetric Titration	Sulfanilic acid, naphthylamine hydrochloride method.
Nitrate Nitrogen	Yes	-do-	Brucine method
Total Dissolved Solids	Yes	Gravimetric	--
Temperature	Yes	Mercury Thermometer	--



plate count, COD, nitrogen (ammonia, organic,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ), pH and ORP, on the influent and effluent of the filters. After this period of continuous operation, considerable slime growth was observed in the filters, oxygen was being depleted in the filter influent as it passed through the filters and ferrous iron was found in the finished water. The filters were backwashed at 48-hour intervals; generally the head loss in the filters at that time was about 5 feet of water. It was observed that even with a backwash rate as high as  $12 \text{ gpm/ft}^2$  it was not possible to clean the slime from the filters completely. Occasionally sand balls formed which had to be broken manually.

When the filters were "ripened," and were passing considerable amounts of ferrous iron, studies were made to determine the pattern of iron breakthrough and the biological growth between backwash cycles or during the filtration period. Samples were taken at various locations of the pilot plant at regular intervals (4 to 6 hours) during a filter run unless otherwise mentioned. The analyses were made according to the following program:

I. Raw water entering aerator

- a) Alkalinity - at 8-hour intervals
- b) Dissolved oxygen
- c) Iron - total and total ferrous
- d) pH
- e) Temperature
- f) Organic nitrogen - at 8-hour intervals
- g) ORP
- h) Bacterial count at 8-hour intervals
- i) COD - -do-



j) Nitrogen (ammonia and organic) - -do-

## II. Aerated water

a) Dissolved oxygen

b) Iron - total ferrous and ferrous in solution

c) pH

d) ORP

## III. Settled water (Influent to the filters)

a) Dissolved oxygen

b) Iron - total, ferrous in solution and total ferrous

c) pH

d) ORP

e) Organic nitrogen - at 8-hour intervals

f) Ammonia nitrogen - -do-

g)  $\text{NO}_2^-$  - nitrogen - -do-

h)  $\text{NO}_3^-$  - nitrogen - -do-

i) COD - -do-

j) Bacterial Plate Count - -do-

k) Temperature

l) Alkalinity - at 8-hour intervals

## IV. Filtered water

The sampling scheme for the effluent from each filter was identical to that for the settled water. Occasionally sand samples at depths 0.25, 3, 9 and 30 inches, and backwash waters from the filters were collected and analyzed for iron, COD, and organic nitrogen.

Since the amount of nitrogen in any particular sample was small, the samples for the analysis of all forms of nitrogen were acidified as they were collected. This was done in order to control biological nitrification



during the period from the time of collection of the sample to the time of analysis.

After each backwash, the collection of samples was initiated after two volumes of water had passed through the filter.

Minor changes in the sampling program were made when specific data were sought, or when time or manpower were limiting. Occasionally the pilot plant was shut down in order to clean the aerator, the settling tank and the rate-of-flow controllers. The filters were always kept filled with treated water from the Clinton Plant during such times so as to prevent the sand from drying out.

The studies discussed so far were completed during the summer months of 1963 and 1964. From the results of these studies, it was observed that there was a definite pattern of iron breakthrough during a filter run once the filter was "ripened." This was associated with a gradual buildup of a bacterial growth, an increasing rate of depletion of dissolved oxygen and an occurrence of nitrification in the filter.

Therefore, in the second phase of this research which was conducted during the summer months of 1965, studies on the inhibition of bacterial growth were carried out on two 30-inch filters, one of which was a new clean filter and the other a "ripened" one which exhibited all the breakthrough characteristics. It was felt that the inhibition of bacterial growth may offer a solution to the problem of the passage of ferrous iron through the filter. The program of experimentation and sampling was similar to the one followed during the summer of 1964.

Initially, a specific inhibitor for the nitrite-forming bacteria (Nitrosomonas), namely, thiourea, was used to control the activity of this species. The dosages,  $10^{-5}$  to  $10^{-4}$  M, were the same as recommended by



Painter et al. (94). This study was followed by a study of the inhibition of all bacterial growth using the general inhibitor "Roccal."

These inhibition studies revealed that the anaerobic condition and the passage of excessive amounts of ferrous iron was indeed a bacterially mediated process. Therefore, seeking a practical and economical solution to this problem, a chlorination study was undertaken. In this study pre-chlorination and superchlorination of the filters were practiced in order to alleviate the problem.

A chronology of all experimental runs carried out in the course of the research is given in Table 7.

TABLE 7  
CHRONOLOGY OF EXPERIMENTS

Run No.	Period	Purpose	Observation
1-3	June-Sept, 1963	Rate adjustment and elimination of erroneous influences	
4-6	-do-	Normal operation	Head loss, normal breakthrough pattern, etc.
7	-do-	Ripened filters, chemical reduction of iron	Studies on chemical and bacterial influence on iron removal.
8-15	June-Sept, 1964	Normal operation	Head loss, normal breakthrough pattern, etc.
15-21	-do-	Ripened filters	Studies were similar to those for Run 7
22-27	May-Aug, 1965	Ripened filters	Inhibition studies
28-30	-do-	-do-	Studies on chlorination of filters.



#### 4. RESULTS AND DISCUSSION

##### 4.1 Studies on Filters Prior to Ripening

Studies conducted during the summer of 1963, 1964, and 1965 indicated that eight to ten weeks would elapse before reducing conditions would develop in a new, clean experimental filter. This was taken as the ripening period. Studies made each year prior to the ripening of filters were devoted mainly to the determination of the head loss characteristics and pattern of iron breakthrough in filters which had a relatively small amount of biological growth and were operating efficiently.

##### 4.1.1 Effluent Quality and Head Loss Characteristics

Effluent water quality was poor at the beginning of each filter run. Iron concentration in the effluent reached a peak at approximately the theoretical time required to displace the volume of water originally in the filter. The effluent iron content then continually decreased to an equilibrium value.

Figure 13 shows a typical initial breakthrough and improvement in effluent iron content for the 30-inch filter during Run 4. Equilibrium conditions were approached in 50 minutes or the time needed to displace approximately three volumes of water. It also appeared that some oxidation of ferrous iron took place in the initial stages of a filter run. This observation has been reported by Cleasby and Baumann (65) and Ling(60).

Figure 14 shows curves for the concentration of iron in the effluent with time at different filter depths during Run 4. These curves are typical of the results obtained in other filter runs following the initial improvement or equilibration period. As expected, considerable breakthrough of iron was observed at the 3- and 9-inch filter depths after



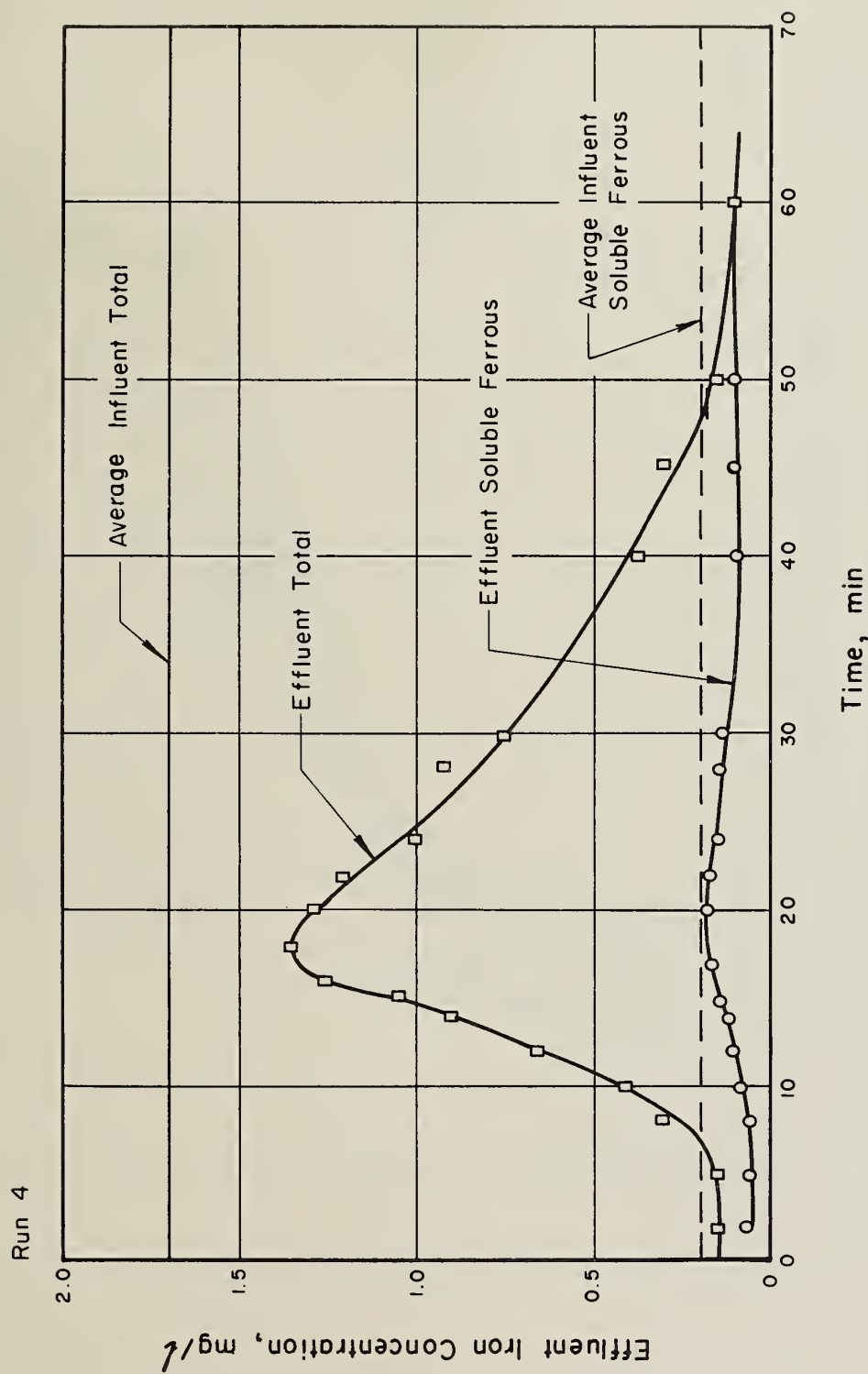


FIGURE 13. INITIAL TIME TO REACH EQUILIBRIUM



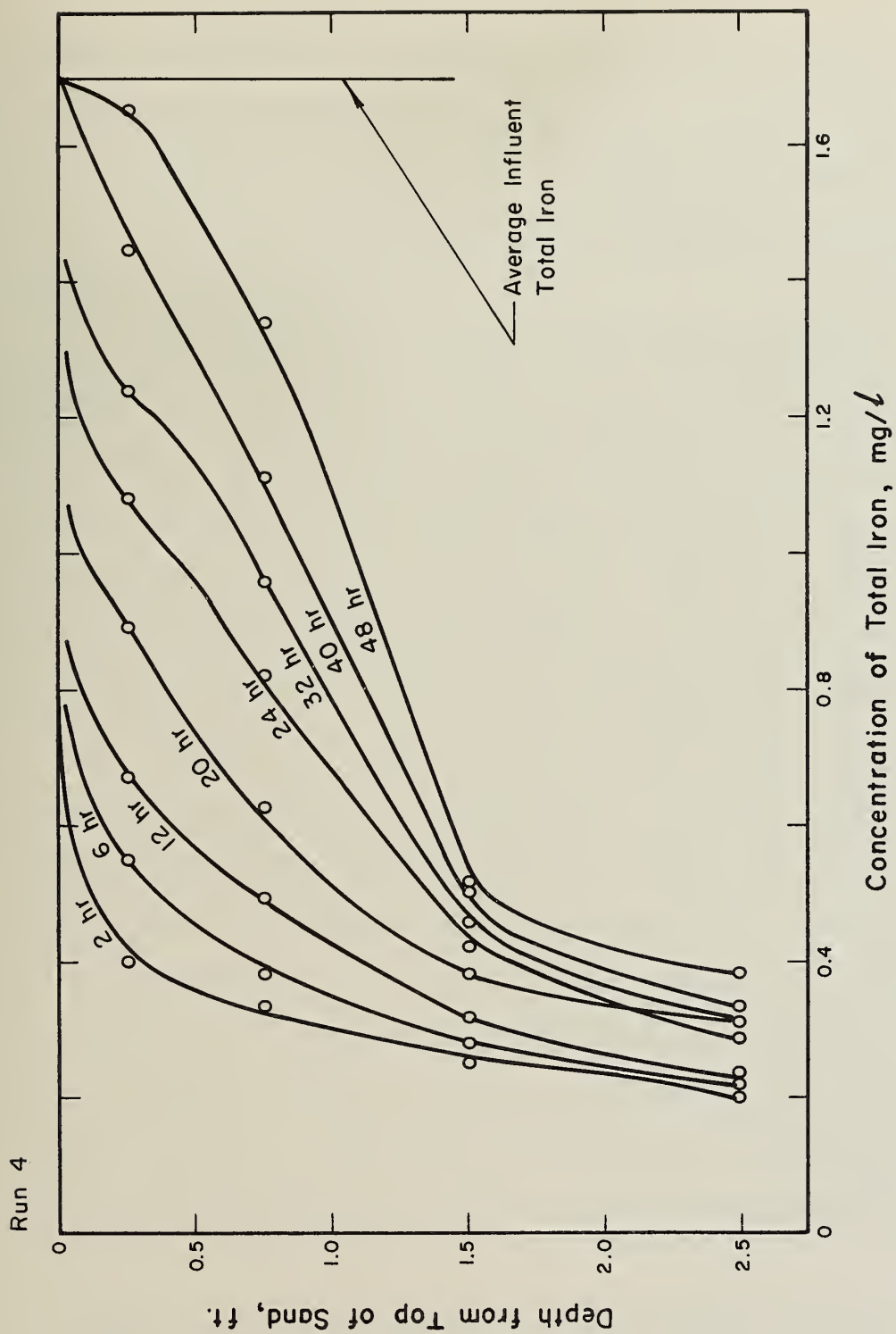


FIGURE 14. EFFLUENT IRON CONTENT DURING A NORMAL RUN



32 hours of operation. The effluent from the 18- and 30-inch deep filters removed iron satisfactorily throughout the run. Similar observations were made by Stein (59) and Eliassen (95) in their studies. As the soluble ferrous iron in the effluent during the run was fairly constant, 0.1 mg/l, it is not shown in Figure 14.

Head loss curves during Run 4 are shown in Figure 15. The rate of increase in head loss at a depth of 18 inches equalled the rate of increase at a depth of 30 inches. This indicated that under normal conditions the pilot plant filter did not remove appreciable amounts of insoluble iron or other suspended matter, e.g.,  $\text{CaCO}_3$ , below a depth of 18 inches. All the filters were backwashed at approximately 48-hour intervals when, generally, the loss of head in the 30-inch filter reached 5.0 to 5.5 feet of water.

Figure 14 indicates that even after 48 hours of operation the 30-inch filter was effectively removing iron. It was of interest to see how long the deeper filters could be operated before a complete breakthrough of iron was observed. Figure 16 shows the breakthrough curves for different depths during Run 9. It is noteworthy that, even after prolonged filtration, the original iron concentration (the influent iron concentration, 1.8 mg/l) was not reached although the effluent iron concentration approached a constant level, nor was zero concentration approached in the beginning. The latter result was due to the presence of the soluble ferrous iron in the influent.

#### 4.1.2 Chemical and Biochemical Characteristics of Water During Normal Filter Runs

The changes in alkalinity, DO, pH,  $E_h$ , iron, nitrogen, COD and bacterial count (standard plate count) that occurred during a filtration period (Run 4) are described in this section.



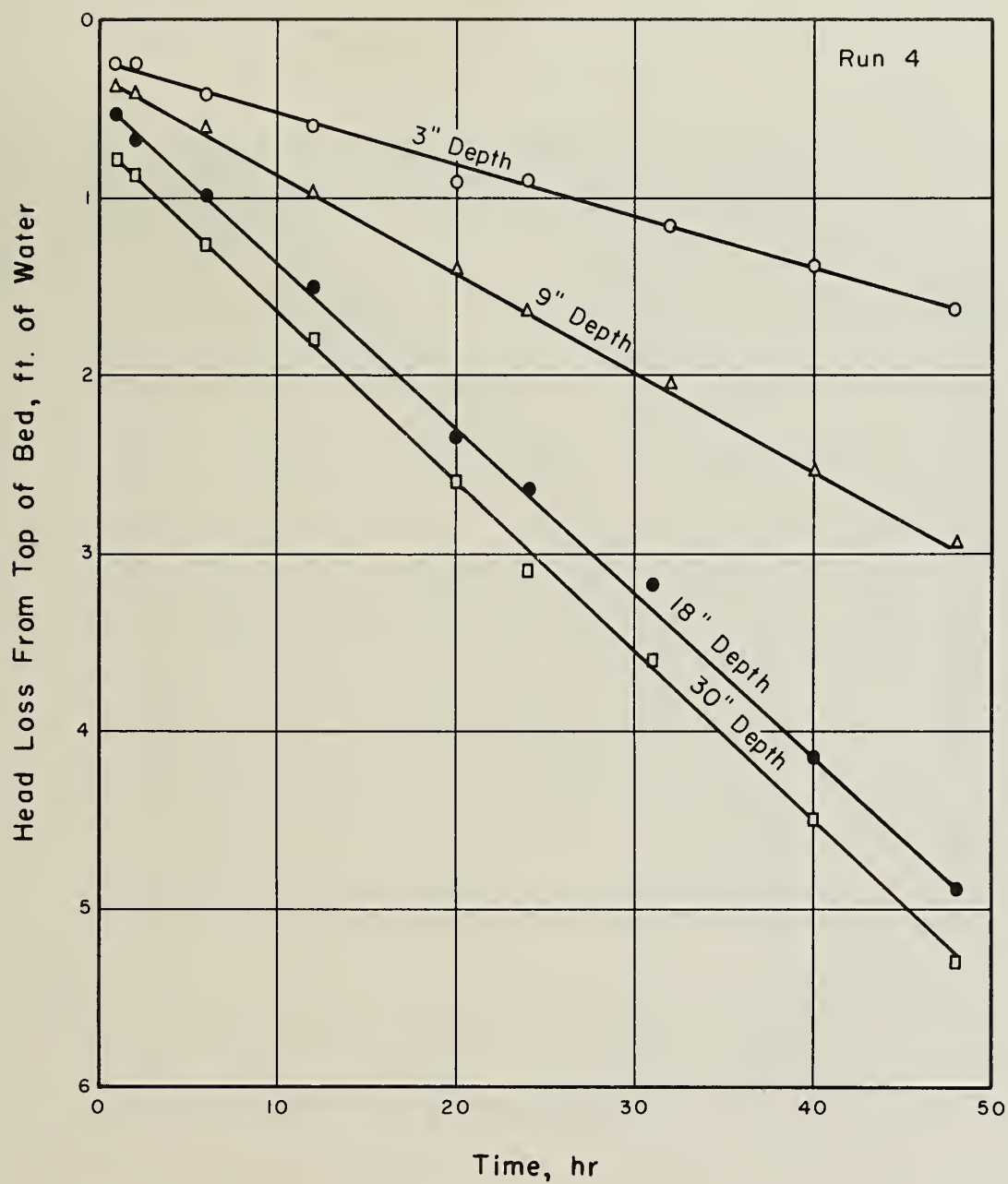


FIGURE 15. HEAD LOSS DURING FILTRATION



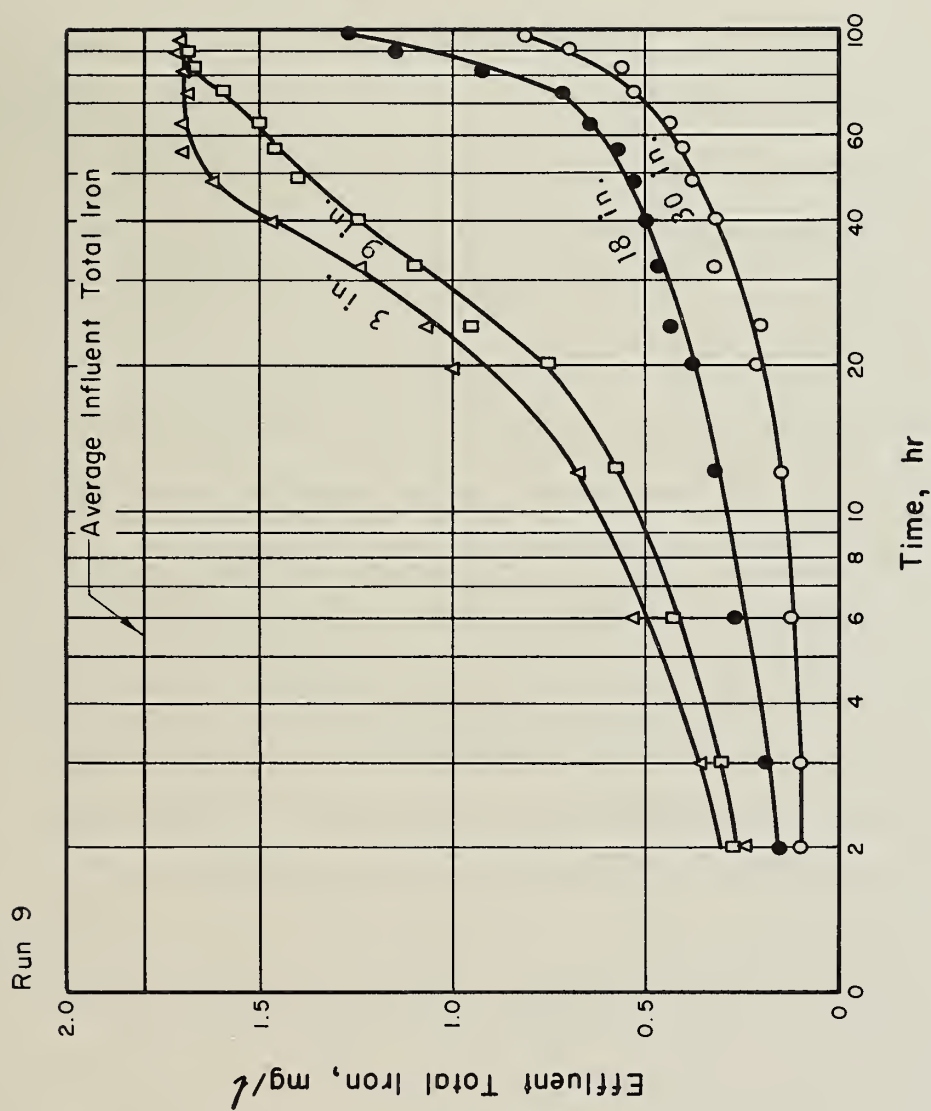


FIGURE 16. BREAKTHROUGH OF IRON



#### 4.1.2.1 Raw and Influent Water

Table 8 shows the quality of the raw and settled water prior to its application to the filters. It can be seen that there was an increase of about 0.4 units in the pH value of the water following aeration and settling. This was due to the stripping of  $\text{CO}_2$  from the water which was originally supersaturated with  $\text{CO}_2$  in the aquifer. The rise in pH caused a decrease in alkalinity due to the precipitation of some hardness producing cations, as carbonates. This can further be confirmed by the decrease in hardness in the settled water as indicated in Table 8.

The organic nitrogen values did not change significantly during settling. Although there was some increase in the bacterial count after settling, the organic nitrogen merely changed its form, i.e., it was incorporated into cell protoplasm. The slight decrease in COD value may have been due to the fact that part of the organic carbon was used in respiration to supply energy for bacterial growth. The bacterial count indicated in Table 8 does not include any nitrifying organisms which cannot grow on nutrient agar. Bacteria were grown on the nutrient agar plates for 48 hours at 25°C. It is of interest to note that probably there was no species of bacteria present in the water capable of fixing nitrogen from the atmosphere. This is indicated by the fact that there was no increase in the organic nitrogen concentration after settling although there was an increase in the bacterial count. Furthermore, there was no evidence of nitrification in the settling tank, since no nitrite and nitrate were found in the settled water.

Although the raw water was totally devoid of oxygen, the aeration device introduced between 6.5 to 7.8 mg/l of DO. There was a small decrease in the DO concentration during settling (0.5 to 0.8 mg/l) which is not shown



TABLE 8

## QUALITY OF RAW AND SETTLED WATER DURING RUN 4

Sample Type	Time, hr	DO, mg/l	pH	E <sub>h</sub> , mv	Alkalinity, mg/l as CaCO <sub>3</sub>	Total Hardness, mg/l as CaCO <sub>3</sub>	Ca Hardness, mg/l as CaCO <sub>3</sub>	Organic N, mg/l	NH <sub>4</sub> -N, mg/l	COD, mg/l	Bacterial Count, no./ml
RAW	2	nil	7.25	+330	440	343	180	3.5	3.2	34	160
	6	nil	7.30	+322	--	--	--	--	--	--	--
	12	nil	7.31	+317	--	--	--	3.8	2.9	32	280
	20	nil	7.27	+328	--	--	--	--	--	--	--
	24	nil	7.28	+325	428	350	184	--	--	--	--
	32	nil	7.22	+328	--	--	--	2.9	3.0	35	210
	40	nil	7.31	+332	--	--	--	--	--	--	--
	48	nil	7.32	+330	434	338	172	3.1	3.1	35	120
SETTLED	2	7.2	7.75	+440	424	328	171	3.6	3.2	25	1,700
	6	7.1	7.68	+432	--	--	--	--	--	--	--
	12	6.8	7.70	+428	--	--	--	3.7	3.0	22	2,200
	20	6.8	7.62	+445	--	--	--	--	--	--	--
	24	6.7	7.58	+418	396	331	173	--	--	--	--
	32	7.3	7.56	+429	--	--	--	3.1	2.8	29	3,100
	40	6.9	7.67	+413	--	--	--	--	--	--	--
	48	7.7	7.55	+438	418	317	161	3.0	2.9	31	2,600



in Table 8. This was most likely due to the oxygen demand exerted by the bacterial growth and the oxidation of ferrous iron in the settling tank.

There was a consistent increase of about 100 mv in the  $E_h$  value of the water following aeration due to the introduction of oxygen.

Figure 17 shows the concentrations of different forms of iron in the raw and settled water as recorded during the course of Run 4. There was no insoluble ferrous iron in the raw water. However, the average concentration of soluble ferrous iron was almost 80 percent of the total iron. In the filter influent, after aeration and detention, the average soluble ferrous iron concentration was about 10 percent of the total iron. The total ferrous iron concentration in the same water was 30 percent of the total iron. In other words, 20 percent of the total iron present in the settled water was some form of ferrous iron which was either insoluble or possibly adsorbed on the insoluble ferric oxide hydrates. Only 40 percent of the total iron in the raw water was removed by aeration and settling. The formation of insoluble ferrous forms, e.g.,  $[\text{FeCO}_3 \cdot \text{Fe}(\text{OH})_2]$ , is theoretically possible in the pH range of the settled water as shown by Figure 4. Approximately 80 percent of the soluble ferrous iron was oxidized prior to filtration during Run 4. The precipitate formed consisted of insoluble ferrous and ferric iron and had poor flocculating properties. The formation of aquo complexes of iron is indicated. Such complexes contribute to the formation of hydrophilic colloids which resist flocculation (Section 2.4).

#### 4.1.2.2 Filtered Water

Figure 18 shows the concentration of iron in the filtered water during Run 4. At depths of 3 and 9 inches the amounts of



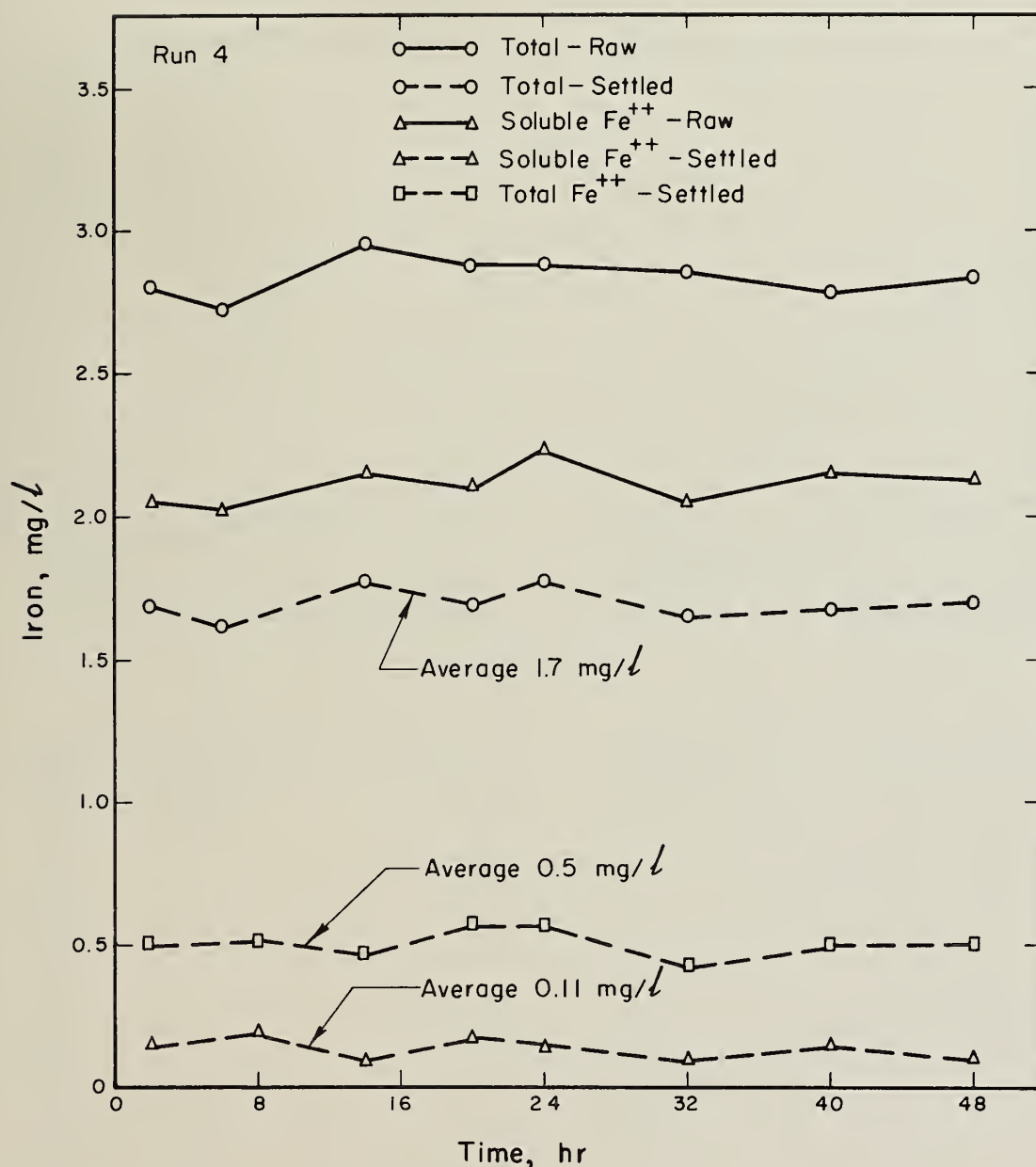


FIGURE 17. IRON CONCENTRATION IN RAW AND SETTLED WATER DURING RUN 4



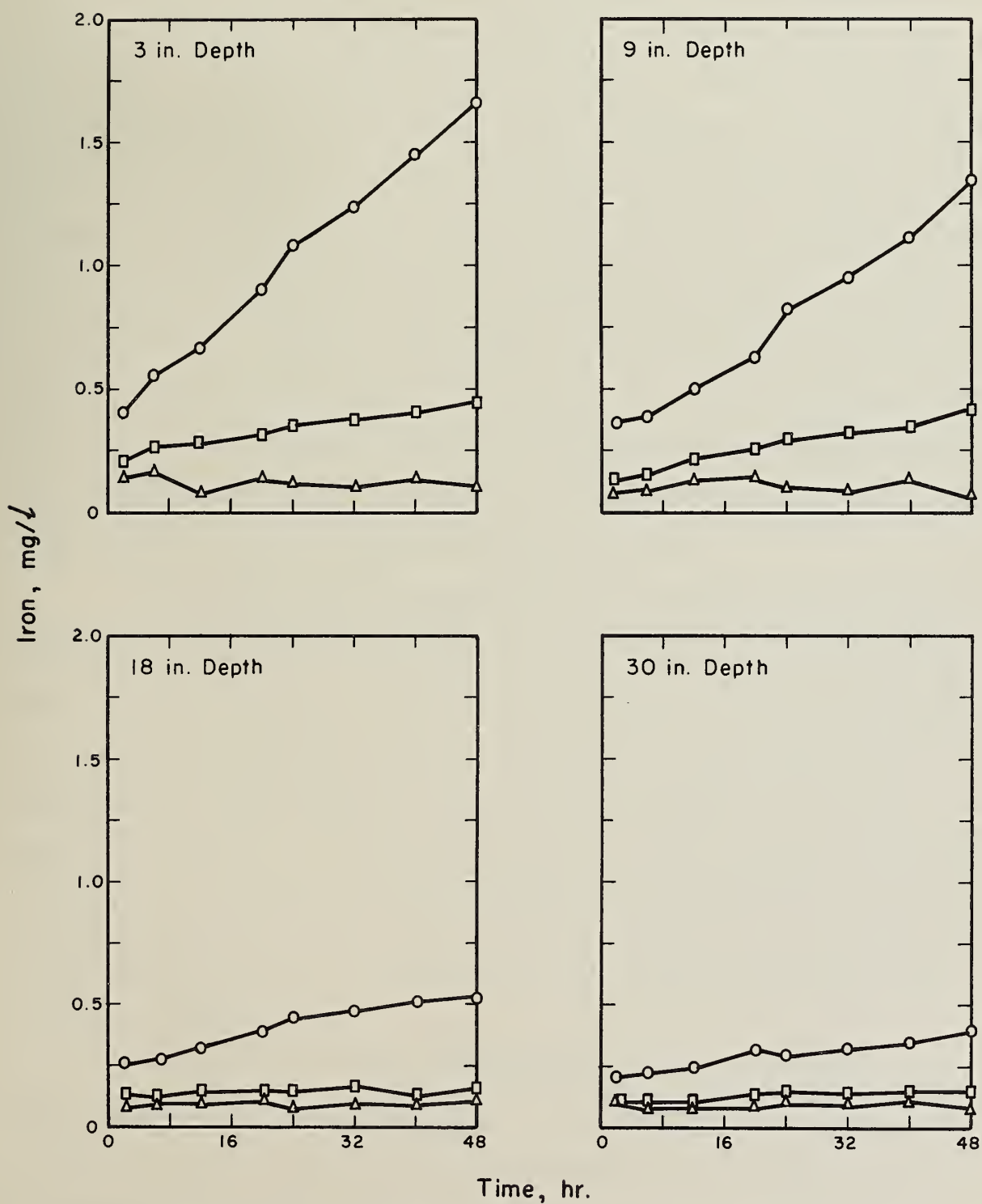


FIGURE 18. IRON CONCENTRATION IN FILTERED WATER



total iron passing through the filter are large and continue to increase throughout the filtration period. Comparing Figure 18 with Figure 17 it appears that under normal conditions there may be a certain amount of oxidation of iron from the ferrous to the ferric form in an aerobic rapid sand filter. However, after 48 hours the amount of insoluble ferrous iron (total ferrous minus soluble ferrous) passed through the 3- and 9-inch depths almost equalled the amount of insoluble ferrous iron in the influent to the filters. This was also true of the insoluble ferric iron (difference between total iron and total ferrous iron). Furthermore, the degree of oxidation of ferrous iron in a filter under aerobic conditions appears to depend on the time of contact of the water with the sand bed. This is apparent from Figure 18. Similar observations have been made by Holluta and Eberhardt (7). The concentration of soluble ferrous iron in the filtered water was low and remained fairly constant during the filtration period.

The quality of the filtered water with regard to DO, pH, ORP, alkalinity, total hardness, nitrogen, COD and standard plate count during Run 4 is shown in Table 9. There was a slight decrease in the DO concentration during filtration due to partial oxidation of ferrous iron in the filters and the demand exerted by the bacterial population. At filter depths of 18 and 30 inches the DO depletion was somewhat greater than that at depths of 3 and 9 inches. This indicates more oxidation of ferrous iron and more bacterial growth in the 18- and 30-inch deep filters than in the 3- and 9-inch deep filters.

The pH did not change significantly in any of the filters. However, there was a slight upward trend in  $E_h$  values during filtration. The hardness decreased slightly indicating precipitation of hardness producing cations (Ca, Mg) in the filters. The influent water was unstable, i.e.,



TABLE 9  
QUALITY OF FILTERED WATER DURING RUN 4

Depth, in	Time, hr	DO, mg/l	pH	E <sub>h</sub> , mv	Alkalinity, mg/l as CaCO <sub>3</sub>	Total Hardness, mg/l as CaCO <sub>3</sub>	Ca Hardness, mg/l as CaCO <sub>3</sub>	Nitrogen, Organic	Ammonia mg/l	COD, mg/l	Bacterial Count, no./ml
3	2	6.5	7.80	+442	410	331	172	2.7	3.2	20.1	1,730
	6	6.5	7.65	+458							
	12	6.3	7.70	+452				2.5	3.0	22.0	2,800
	20	6.4	7.62	+453							
	24	6.2	7.55	+445	388	342	181				
	32	6.5	7.58	+457				3.5	3.2	28.0	7,200
	40	6.8	7.65	+462							
	48	7.1	7.53	+453	412	327	165	4.1	3.1	32.0	7,800
9	2	6.3	7.70	+440	410	315	162	1.2	2.8	7.0	560
	6	6.5	7.63	+445							
	12	6.4	7.71	+458				1.3		18.2	1,250
	20	6.0	7.63	+453					2.8		
	24	6.1	7.54	+455	386	324	178				
	32	6.2	7.41	+463				2.0	3.2	20.8	1,800
	40	6.3	7.53	+453							
	48	6.4	7.58	+453	410	306	163		3.1	21.3	2,300



TABLE 9 (cont.)

## QUALITY OF FILTERED WATER DURING RUN 4

Depth, Time, DO, pH	E <sub>h</sub> , mv	Alkalinity, mg/l as CaCO <sub>3</sub>	Total Hardness, mg/l as CaCO <sub>3</sub>	Ca Hardness, mg/l as CaCO <sub>3</sub>	Nitrogen, mg/l Organic Ammonia	COD, mg/l	Bacterial Count, no./ml		
18	2 6.2 7.65	+438	408	312	158	1.0	2.8	6.5	430
	6 6.2 7.70	+447	---	---	---	---	---	---	---
	12 6.1 7.62	+465	---	---	---	1.2	2.9	17.2	1,120
	20 6.0 7.58	+468	---	---	---	---	---	---	---
	24 5.9 7.53	+472	386	318	165	1.8	3.1	20.2	1,700
	32 6.0 7.43	+461	---	---	---	---	---	---	---
	40 6.1 7.50	+478	---	---	---	---	---	---	---
	48 5.8 7.57	+474	410	304	163	1.9	3.2	21.1	1,850
30	2 6.1 7.53	+448	402	310	161	nil	3.0	6.4	440
	6 6.0 7.58	+452	---	---	---	---	---	---	---
	12 6.0 7.69	+463	---	---	---	1.1	---	8.7	960
	20 5.3 7.61	+478	---	---	---	---	---	---	---
	24 5.8 7.59	+463	384	310	175	1.3	2.8	17.0	1,130
	32 5.9 7.43	+458	---	---	---	---	---	---	---
	40 5.7 7.58	+468	---	---	---	---	---	---	---
	48 5.8 7.60	+460	408	296	160	1.7	3.0	20.0	1,620



supersaturated with calcium carbonate as shown below. The calculations are based on the theories presented in Fair and Geyer (34).

$$pH_s = \log \frac{K_s}{K_2} - \log [Ca^{++}] - \log [A] + 6.301 + S \quad 37$$

where,  $pH_s$  = Saturation pH

$$K_s = 4.82 \times 10^{-9}$$

$$K_2 = 4.69 \times 10^{-11}$$

$Ca^{++}$  = Calcium concn. in meq/l

A = Alkalinity in meq/l

S = Salinity correction

$$= \frac{2.5 \sqrt{\mu}}{1 + 5.3 \sqrt{\mu} + 5.5 \mu}$$

$$\text{and, } \mu = 2.5 \times 10^{-5} S_d$$

( $S_d$  = total dissolved solids in mg/l,

= 500 mg/l for Clinton water.)

$$\text{Therefore, } \mu = 2.5 \times 10^{-5} \times 500$$

$$= 1.25 \times 10^{-2}$$

$$\text{and } S = \frac{2.5 \sqrt{1.25 \times 10^{-2}}}{1 + 5.3 \sqrt{\mu} + 5.5 \mu}$$

$$= 16.8 \times 10^{-2}.$$

Equation 37 reduces to,

$$pH_s = 8.313 - \log [Ca^{++}] - \log [A] + 16.8 \times 10^{-2}$$

The average values for  $[Ca^{++}]$  and  $[A]$  in the influent during

Run 4 were 3.34 meq/l and 8.26 meq/l respectively.



$$\begin{aligned}
 \text{Therefore, } \text{pH}_s &= 8.481 - \log [3.34] - \log [8.26] \\
 &= 8.481 - 0.524 - 0.916 \\
 &= 7.04
 \end{aligned}$$

The average observed pH in the filter influent during Run 4 was 7.64.

$$\begin{aligned}
 \text{Therefore, saturation index, } I &= \text{pH} - \text{pH}_s \\
 &= 7.64 - 7.04 \\
 &= 0.6.
 \end{aligned}$$

This indicates that the water was supersaturated with  $\text{CaCO}_3$  (or lacking in excess  $\text{CO}_2$ ) and some precipitation of  $\text{CaCO}_3$  was to be expected in the filters.

There was a gradual increase in the bacterial population in the filters during the filtration period as indicated by the bacterial counts in the effluent samples shown in Table 9. A larger number of bacteria were being passed at depths of 3 and 9 inches than at 18 and 30 inches at any given time. This indicated that some bacteria were being retained in the filter at depths greater than 9 inches. The effluent concentrations of organic nitrogen and COD were less at depths of 18 and 30 inches than at depths of 3 and 9 inches. This would indicate that most of the bacteria were being removed in the deeper filters. There was no evidence of nitrification in the filters, however.

Table 10 shows the results of an analysis of the backwash waters from the filters at the conclusion of Run 4. The total volume of water used for backwashing was the same for all the filters. The entire volume of the backwash water from each filter was collected in a bucket and thoroughly mixed prior to the pipetting of samples for analysis. The iron removed by the sand bed at different depths had a ferrous iron fraction which varied from 9.1 to 19.0 percent depending on the depth of the filter. The greater the depth, the higher was the degree of oxidation. No soluble ferrous iron



could be found in the supernatant of centrifuged samples of the backwash water. The COD and organic nitrogen values shown in Table 10 appear to be related to the bacterial growth in the filters.

TABLE 10  
ANALYSIS OF BACKWASH WATER AT THE CONCLUSION OF RUN 4

Filter	Iron, mg/l		Percent Ferrous	COD, mg/l	Organic-N, mg/l	Bacterial Count, no./ml
	Total	Total Ferrous				
3 in.	260	49	19.0	16.7	1.2	6,300
9 in.	280	48	16.7	24.6	1.8	11,300
18 in.	344	34	9.8	32.8	2.1	12,800
30 in.	362	32	9.1	41.5	3.2	16,200

#### 4.2 Studies on Ripened Filters

Through three summers the filters were operated for 8 to 10 weeks before any significant depletion of dissolved oxygen in the filter effluent was observed. This DO depletion was accompanied by the formation of nitrite ( $\text{NO}_2^-$ ), nitrate ( $\text{NO}_3^-$ ), slight decreases in pH,  $E_h$ , and alkalinity, and a reduction of iron from the ferric to the ferrous state. A progressive build-up of biological growth was observed in the filters which could not be washed off the sand grains even with prolonged backwashing at rates between 10 to 12 gpm/sq ft.

Filter Runs 15 to 21 were made when the filters were ripened. The general observations outlined in the preceding paragraph were made during each filter run. The results from several typical filter runs using ripened filters are discussed in the following sections.



#### 4.2.1 Chemical and Biochemical Characteristics of Water During Filtration Through Ripened Filters

##### 4.2.1.1 Raw and Influent Water

The average quality of the raw water and filter influent, aerated and settled, was much the same as during Run 4. The results of the analysis of the raw and settled water during two consecutive filtration periods, Run 16 and Run 17, are graphically represented in this section.

Figure 19 shows the concentrations of the various forms of iron in the raw and settled water during Runs 16 and 17. The degree of oxidation of soluble ferrous iron and the degree of precipitation of the insoluble forms of iron were about the same as described for Run 4 in Section 4.1.2.1 (Figure 17).

Figure 20 shows the variation of hardness, alkalinity,  $E_h$  and pH of the raw and settled water during Runs 16 and 17. The pH and  $E_h$  values of the water increased following aeration and settling due to the liberation of  $\text{CO}_2$  and the introduction of oxygen. The hardness and alkalinity values are slightly lower in the settled than in the raw water. This is due to the precipitation of some hardness-producing cations resulting from an increase in pH.

Figure 21 shows the DO, organic nitrogen and COD content of the settled water. The COD of the settled water was slightly less than that of the raw water. This was probably due to the fact that a fraction of the organic matter in the raw water was synthesized into cell protoplasm. A part of the cell mass, thus formed, settled out in the reaction-sedimentation tank. The increase in the bacterial population is evident from Figure 22 which shows the variation in the bacterial population in the raw and settled water during the course of Run 16. It should be noted, however, that



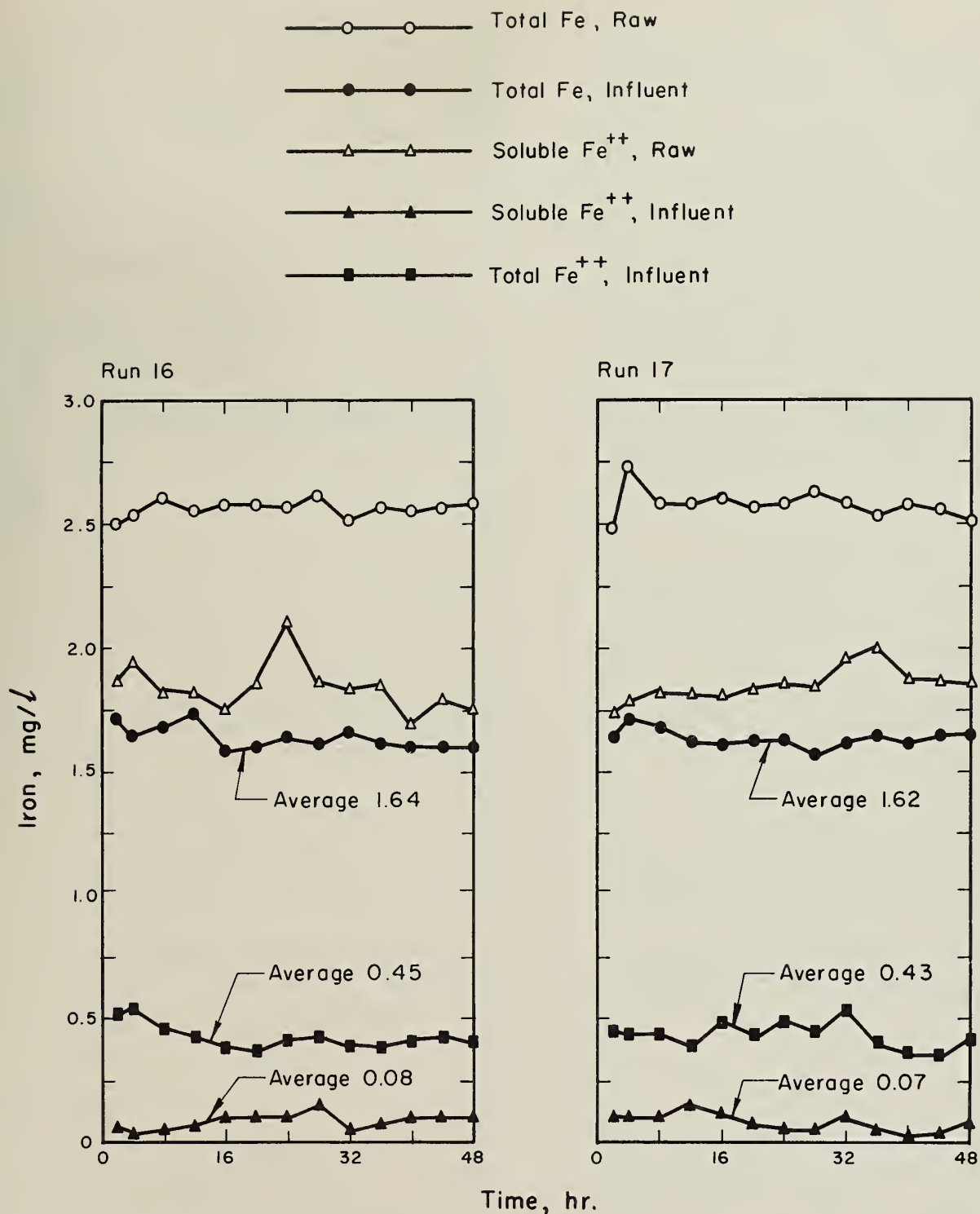


FIGURE 19. IRON CONCENTRATION IN RAW AND SETTLED WATER



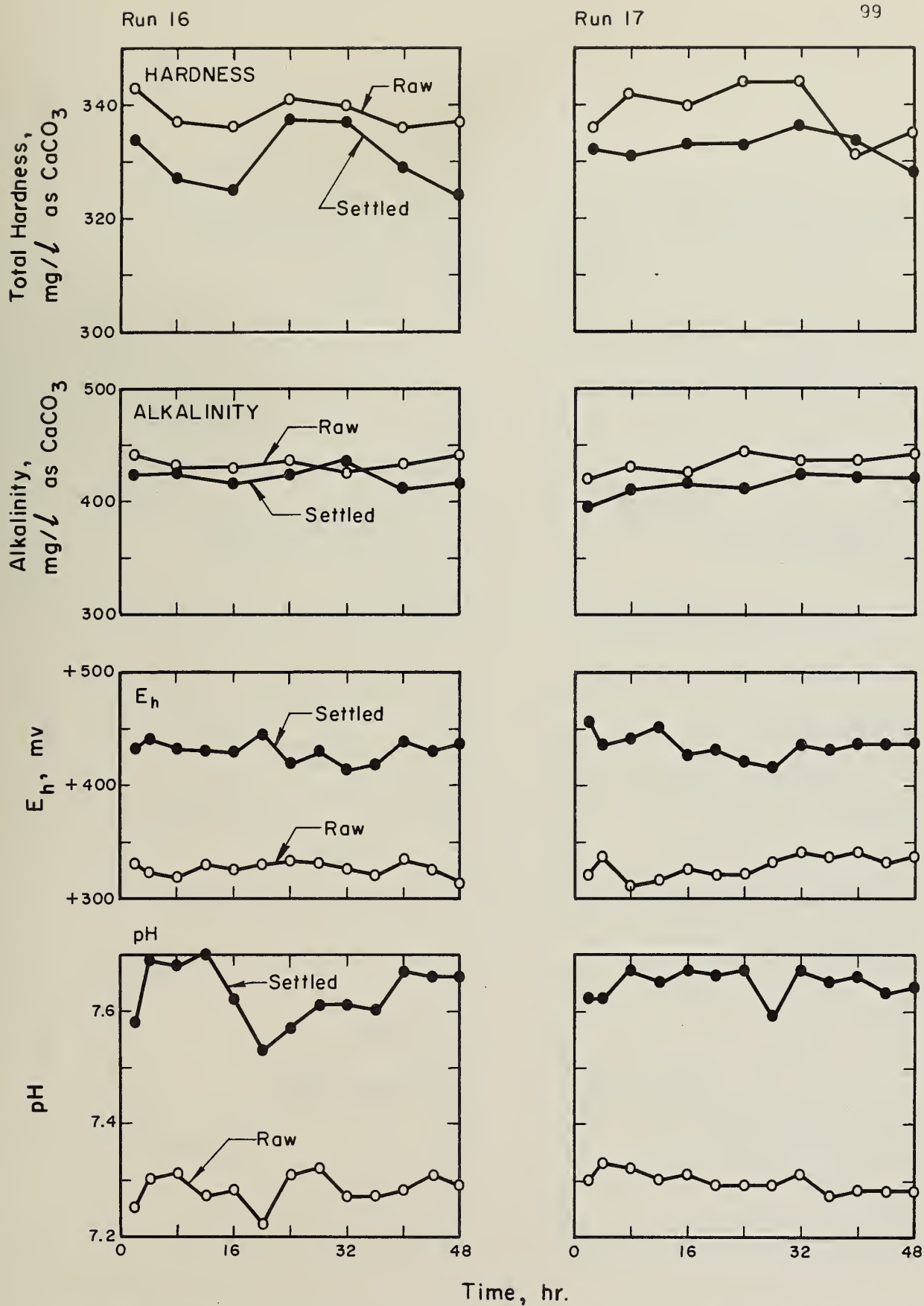


FIGURE 20. HARDNESS, ALKALINITY,  $E_h$  AND pH OF RAW AND SETTLED WATER



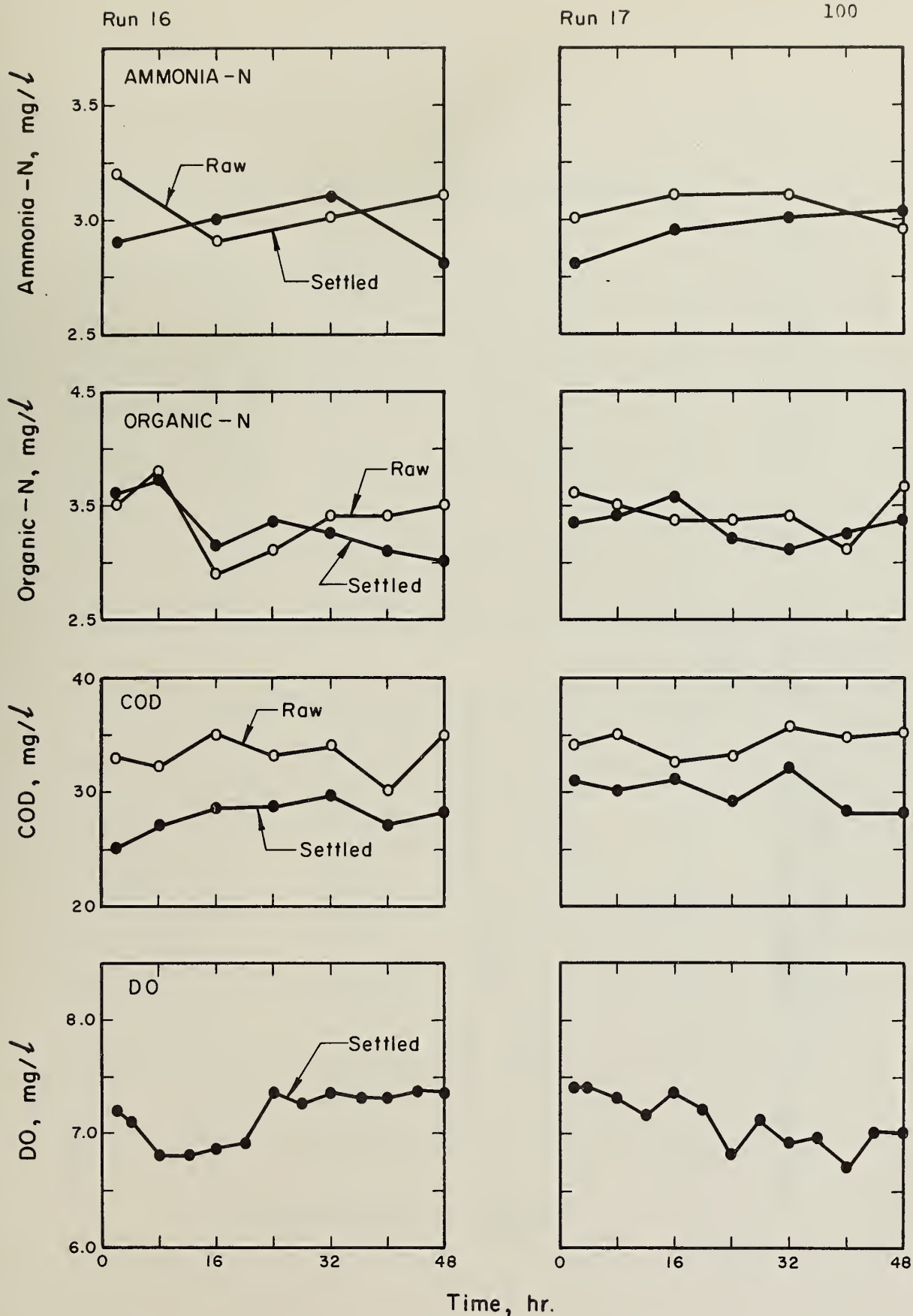
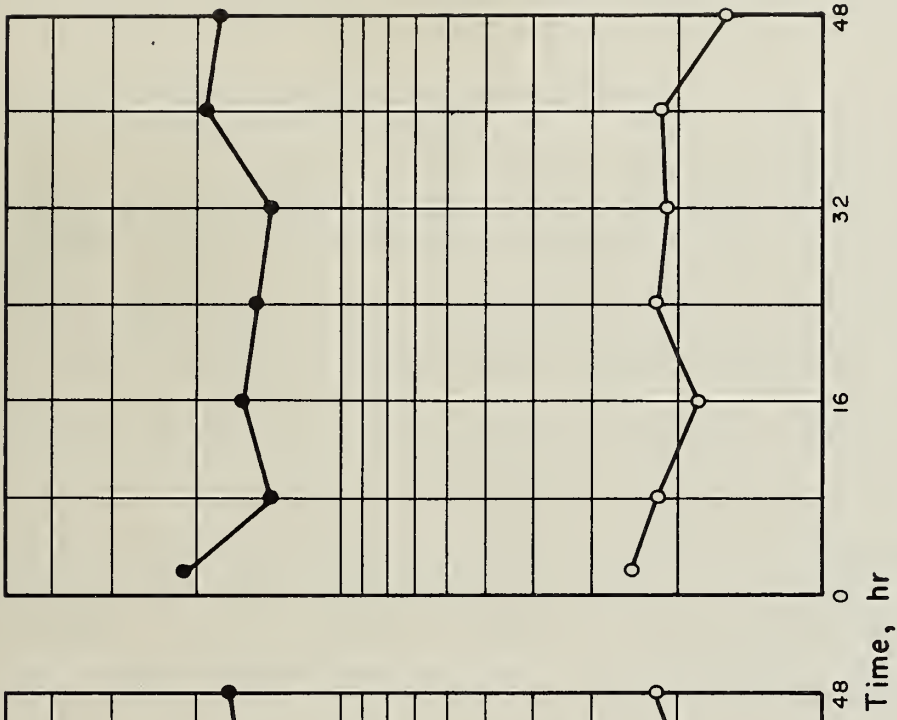


FIGURE 21. DO, COD, ORGANIC-N AND AMMONIA-N CONTENT IN RAW AND SETTLED WATER



Run 17



Run 16

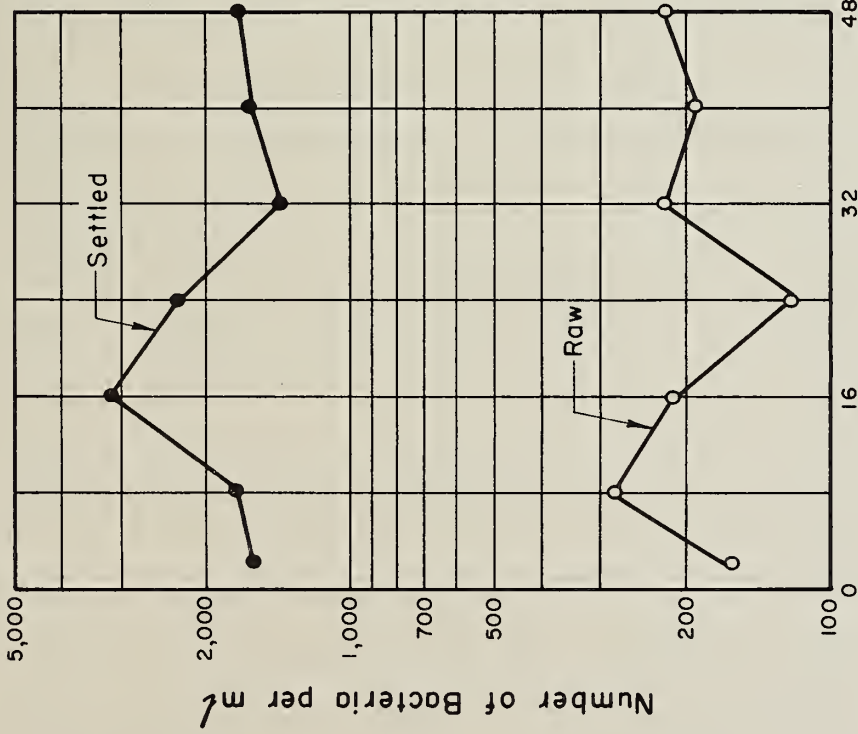


FIGURE 22. NUMBER OF BACTERIA PER MILLILITER IN RAW AND SETTLED WATER



a major fraction of the COD originally present in the raw water remained in solution in the settled water and was not utilized for bacterial growth.

#### 4.2.1.2 Filtered Water

Figures 23 and 24 show the concentrations of the various forms of iron in the effluent from the filters during Runs 16 and 17. The average influent iron concentrations are also indicated on these figures. It is evident that there was a gradual increase in the iron concentration in the filtered water with an increase in time of filtration.

The concentration of total iron in the effluent from the 3- and 9-inch filters was higher than that from the 18- and 30-inch filters. On the other hand, the total ferrous fraction in the effluent from the 18- and 30-inch filters was much higher than that from the 3- and 9-inch filters after about 16 hours of operation. At the beginning of the filter run, the total ferrous iron concentration in the effluent from all the filters was lower than that present in the influent. This indicated that in a relatively clean filter, immediately following backwash, there was evidence of iron oxidation. A definite breakthrough of iron was evident after about 16 hours in all the filters. In the case of the 3- and 9-inch filters, the iron being passed was mostly ferric in form, whereas the 18- and 30-inch filters were passing ferrous iron in both the soluble and insoluble forms. The soluble iron concentration in the effluent from the 3- and 9-inch filters was not higher than that in the influent at any given time. On the other hand, there was a gradual increase in the concentration of soluble ferrous iron in the effluent from the 18- and 30-inch filters as the filtration progressed. After 16 to 18 hours of operation, the soluble iron concentration in the effluent from the 18- and 30-inch filters was higher than that



Run 16

—○—○— Total Fe  
 —□—□— Total Fe<sup>++</sup>  
 —△—△— Soluble Fe<sup>++</sup>

— Average Influent Total Fe  
 - - - Average Influent Total Fe<sup>++</sup>  
 - - - Average Influent Soluble Fe<sup>++</sup>

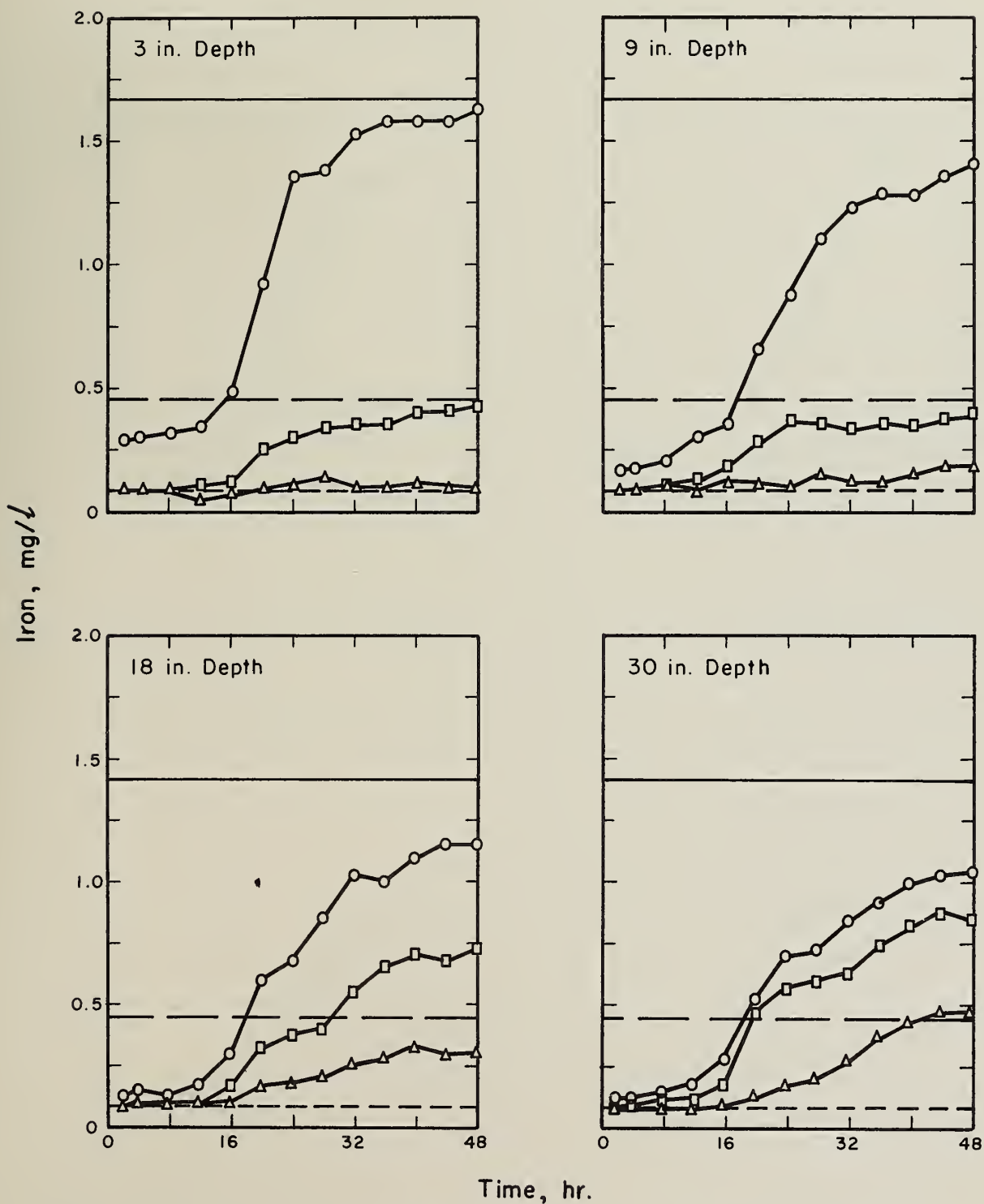


FIGURE 23. IRON CONCENTRATION IN FILTERED WATER



Run 17

104

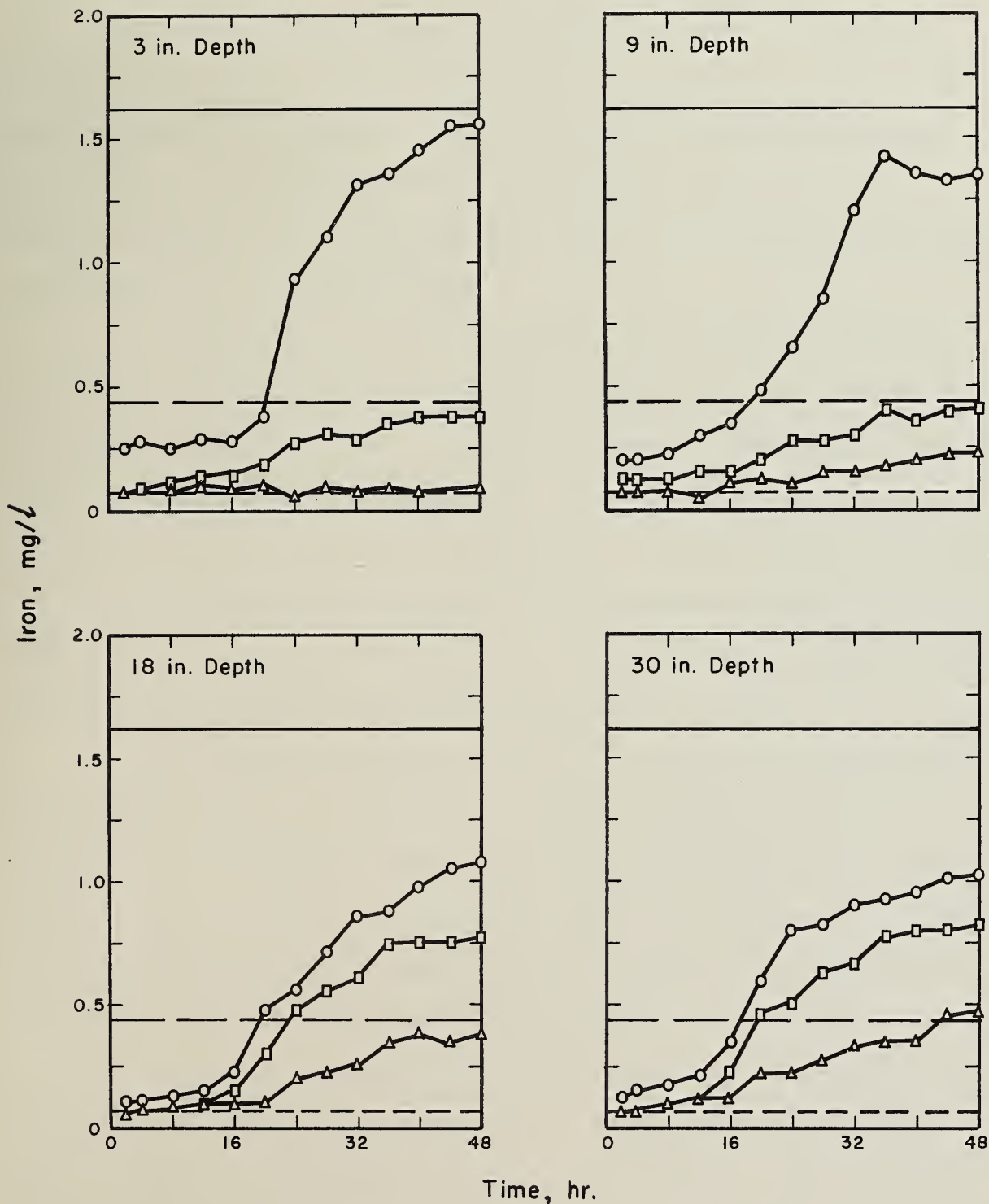
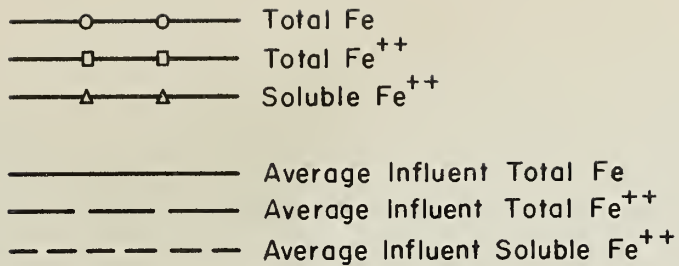


FIGURE 24. IRON CONCENTRATION IN FILTERED WATER



present in the influent.

The total ferrous iron concentration (soluble ferrous plus precipitated or adsorbed ferrous iron) in the effluent from the 3- and 9-inch filters never exceeded that in the influent. However, after 20 to 24 hours, the ferrous iron in the effluent from the 18- and 30-inch filters exceeded that in the influent. This indicated that a reduction of iron from the ferric to the ferrous form was occurring in the filters. It therefore appeared that at depths greater than 9 inches reducing conditions had developed in the ripened filters.

The passage of insoluble iron through the filters was possibly due to the colloidal nature of the insoluble species of iron. In view of the penetrating ability of such a colloid, a depth of filter medium less than 18 inches appears to be insufficient. Studies which have indicated this result have been reported on by Ghosh (96) and Engelbrecht et al. (97).

The concentration of total iron versus depth of filter at various times is shown in Figure 25 for Run 16. After 16 hours of filtration, the ripened filters began passing substantial quantities of iron.

The quantity of insoluble iron in the effluent from the filters during Run 16 is shown in Figure 26. A comparison of Figures 25 and 26 indicates that a large part of the iron passing through the filters was in solution. In addition, Figure 25 reveals that, up to 16 hours of filtration, the filters were effective in removing the insoluble portion of the iron. Thereafter, insoluble iron began to break through.

The typical pattern of the breakthrough of total iron and of insoluble iron is illustrated by Figure 27. A comparison of the curves shown on Figure 27 with Figures 14 and 16 which illustrate the breakthrough of iron in the unripened filters during Runs 4 and 9 shows that the ripened



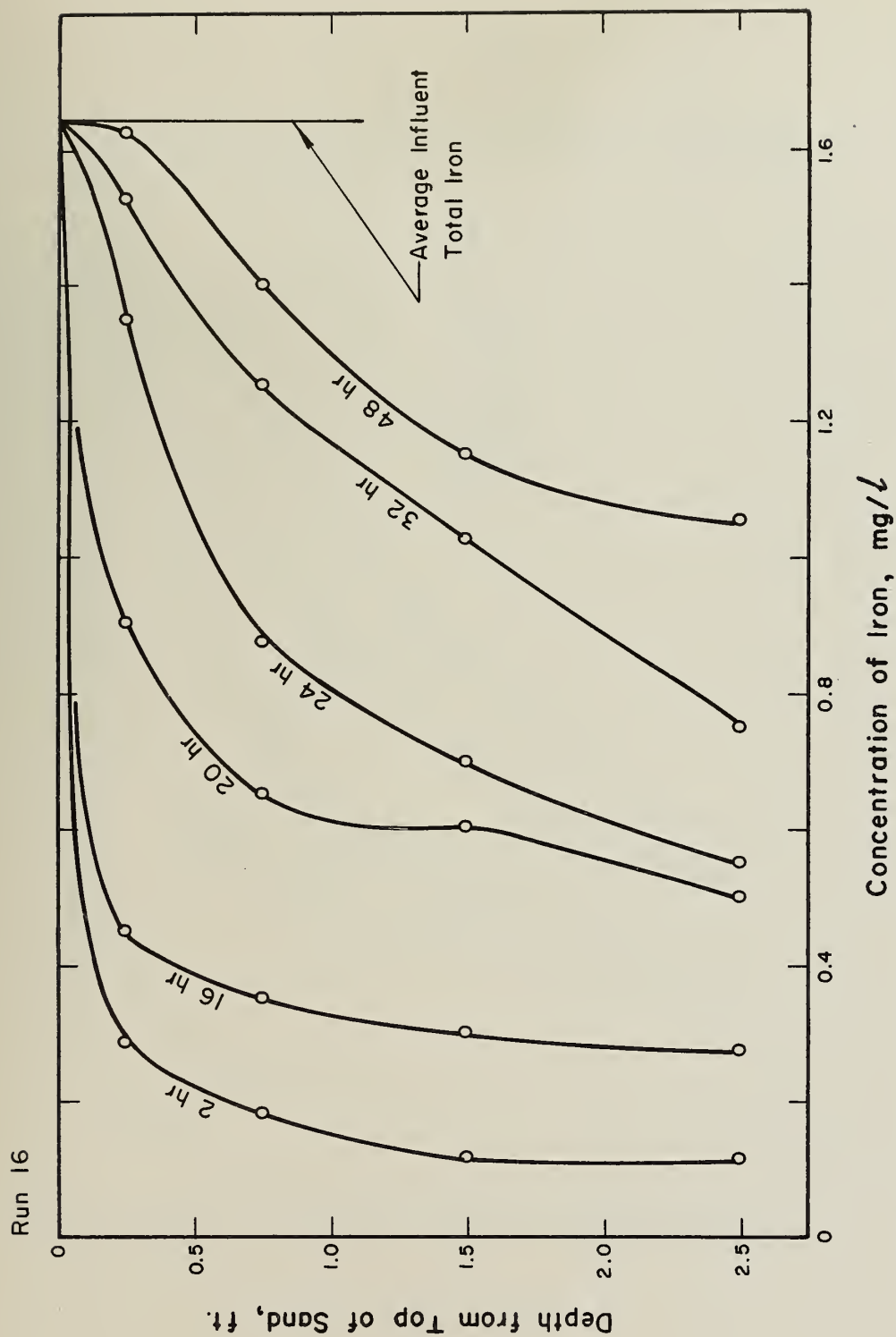


FIGURE 25. EFFLUENT TOTAL IRON CONTENT DURING RUN 16



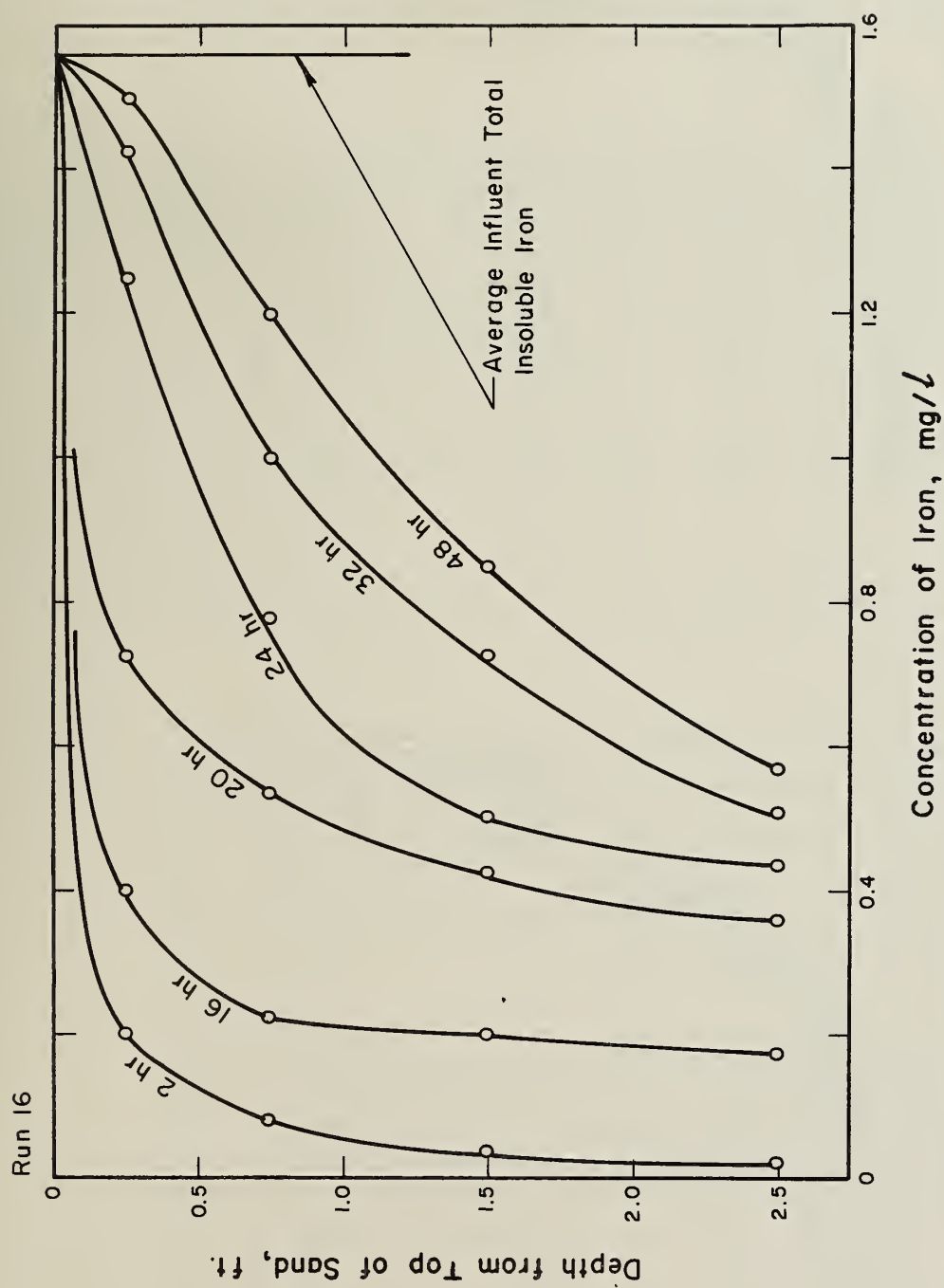
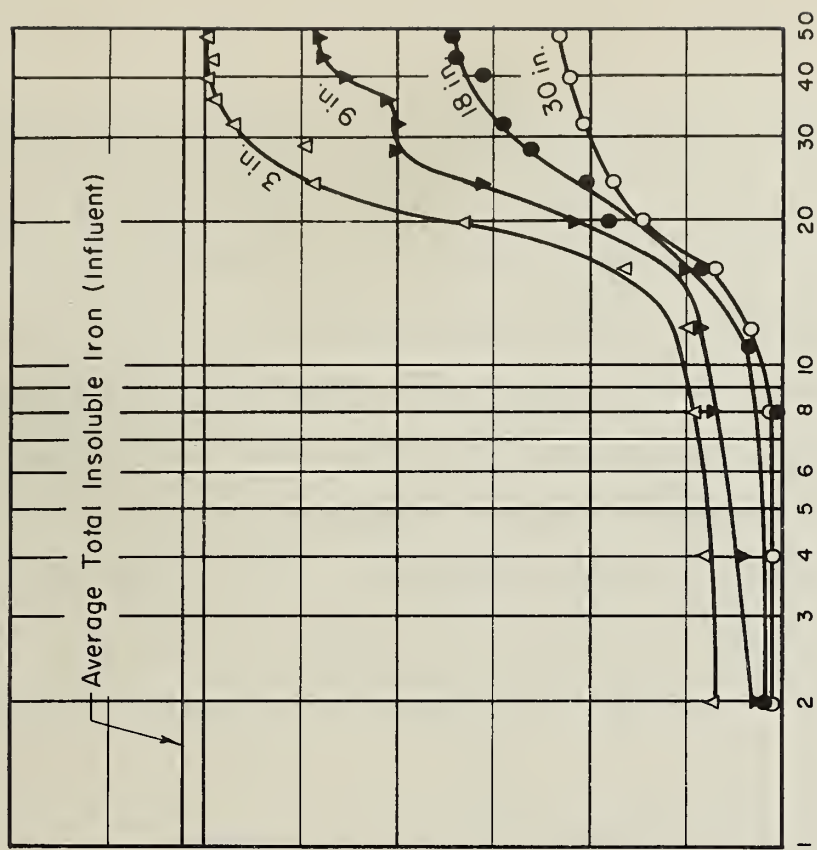


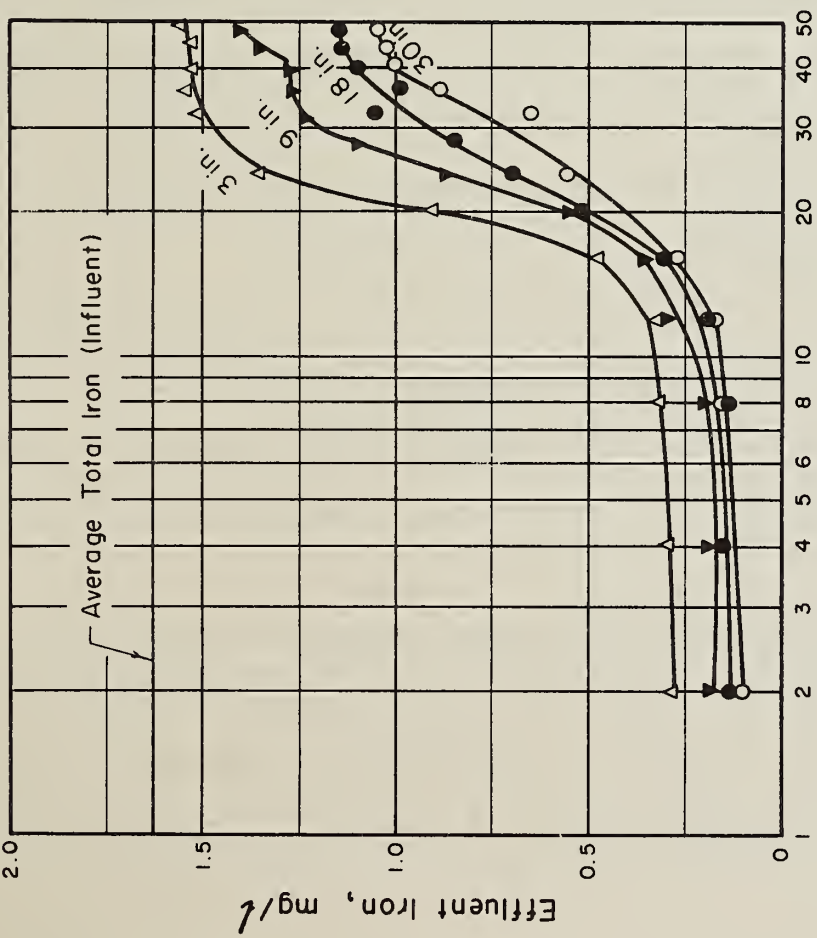
FIGURE 26. EFFLUENT TOTAL INSOLUBLE IRON CONTENT DURING RUN 16



B. Total Insoluble Iron



A. Total Iron



Time, hr

FIGURE 27. BREAKTHROUGH OF IRON DURING RUN 16



filters were at least as effective in removing iron up to 16 hours of operation. In fact, it appears that the ripened filters were clearly more effective than the unripened filters up to that point. This was possibly due to the fact that the sand grains of the ripened filters were coated with iron oxides and slime growths which improved filtration efficiency. Some investigators have credited this increased efficiency of filtration in ripened filters to the phenomenon of surface catalysis on sand grains coated with iron oxides (7). It is readily apparent, however, that the detrimental influence of the biological growth on the filtration of iron is not experienced in the initial stages of filtration.

#### 4.2.1.3 Evidence of Nitrification and Its Effect on Filtration

Once the filters were ripened, it was observed that the concentration of ammonia nitrogen in the effluent from all the filters decreased gradually with an increase in time of filtration. Furthermore, the decrease in ammonia nitrogen was marked by a proportional increase in the nitrite and nitrate nitrogen concentration in the filter effluent. At the same time, there was a depletion of DO, a decrease in  $E_h$  and pH, and an increase in the concentration of iron in the effluent.

The following discussion is devoted to the changes in the chemical and biochemical environment within a ripened filter and to the effect of such changes on filter performance. For brevity, the discussion is confined to Run 16.

Figure 28 shows the ammonia, nitrite and nitrate nitrogen, and the DO concentration in the effluent from the filters. The corresponding influent concentrations are also indicated on Figure 28.

After two hours of operation, half of the influent DO was depleted



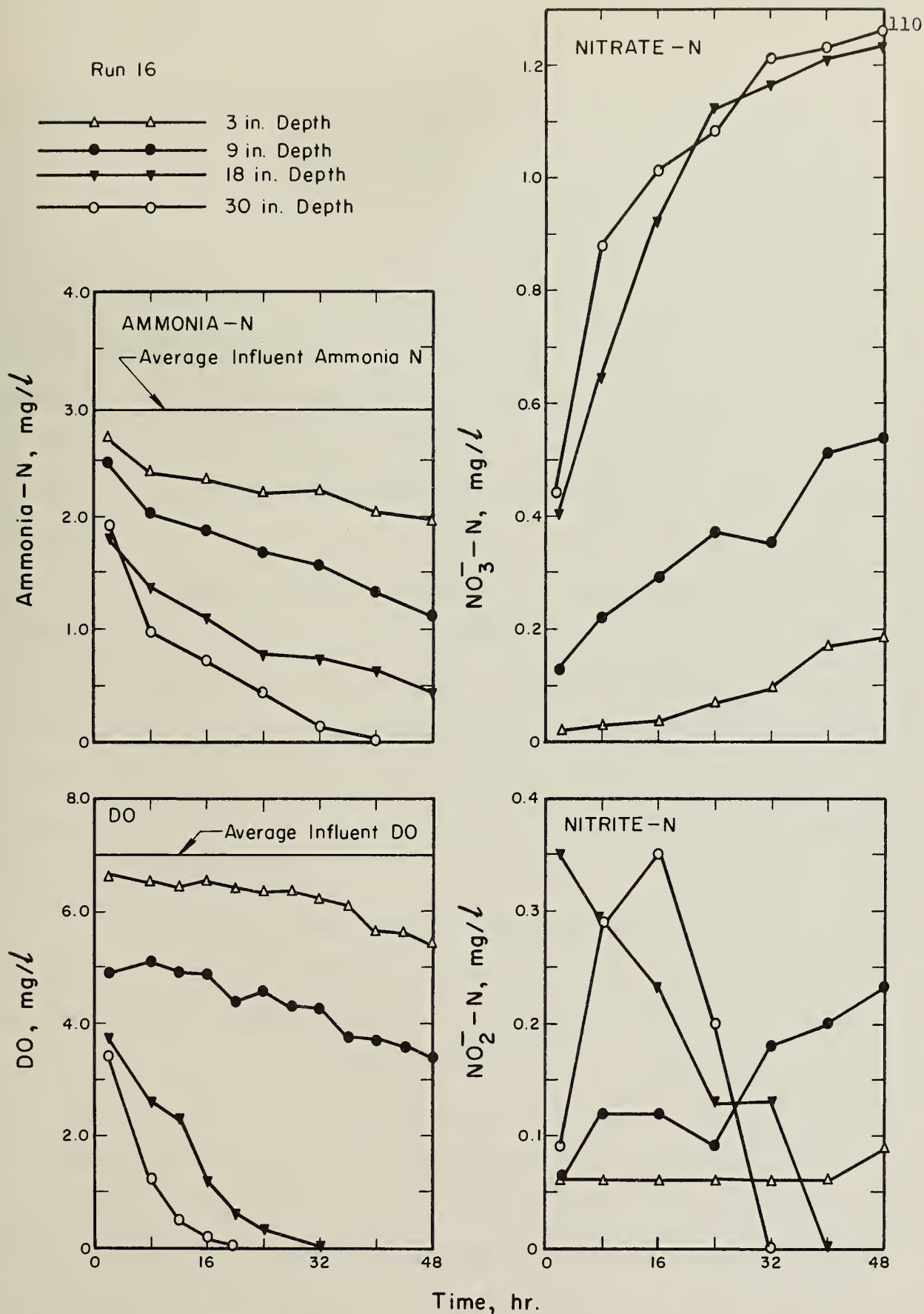


FIGURE 28. EFFECT OF NITRIFICATION ON DISSOLVED OXYGEN CONTENT OF FILTER EFFLUENT



in the 18- and 30-inch filters. The effluents from these filters were completely devoid of DO. Recalling Figure 23, it can be seen that, at about the same time, reduction of iron from the ferric to the ferrous form was initiated in the 30-inch as well as in the 18-inch filter.

The DO content of the effluents from 3- and 9-inch filters was 5.5 and 3.4 mg/l, respectively, after 48 hours. Therefore the maximum depletions during the entire period of filtration were 1.5 and 3.6 mg/l for the 3- and 9-inch filters, respectively. Consequently, no reduction of iron from the ferric to the ferrous form was observed in either of these filters.

The ammonia nitrogen concentration in the effluent from all filters decreased gradually with an increase in time of filtration. However, the degree of depletion of ammonia nitrogen was related to the depth of the filter. The effluent ammonia nitrogen contents indicated a depletion of approximately 1.0, 2.0, 2.5 and 3.0 mg/l for the 3-, 9-, 18- and 30-inch filters at 48 hours. A correlation between the depletion of DO and ammonia nitrogen is apparent.

The depletion of the ammonia nitrogen and DO concentrations was marked by a concomitant increase in the concentration of nitrite and nitrate nitrogen in the effluent as shown in the same figure. The degree of nitrification was least in the 3-inch filter. Furthermore, at any given time, the concentration of nitrite nitrogen was less than the concentration of nitrate nitrogen. The nitrite concentration in the effluent from the 18- and 30-inch filters gradually decreased from an initial high value with an increase in filtration time. However, there was a gradual increase in the nitrate nitrogen content in the 9-inch filter effluent while the nitrite nitrogen content in the effluent from the 3-inch filter remained constant.



Regardless of the trend of nitrite formation, the concentration of the nitrate nitrogen steadily increased in the effluent from all the filters. However, at any given time the amount of nitrate nitrogen was related to the depth of the filter. The effluent nitrate nitrogen concentration approached an equilibrium value in the case of the 18- and 30-inch filters after approximately 40 hours. This may have been due to a stabilization of the population of nitrifying bacteria so that any further growth was not being retained in the filter medium.

The correlation between the degree of nitrification and the indicated amount of DO depletion in the 30-inch filter during Run 16 is shown in Table 11. The values for the oxygen uptake in the formation of nitrite and nitrate from ammonia were computed from the observed concentration of nitrite and nitrate using the equations listed in Table 3. The amount of ammonia nitrogen oxidized at any given time was estimated from the observed values for the nitrite and nitrate nitrogen. Thus, it was possible to estimate the unoxidized fraction of the ammonia nitrogen. By subtracting the computed values for the ammonia nitrogen residuals from the corresponding observed residual values, the fraction of ammonia nitrogen that was synthesized into cell material could be estimated. This is shown in Column 7. Except in the initial stages, up to 16 hours, this fraction gradually increased indicating an increase in the bacterial population with time of filtration. The assumption made here was that the balance of ammonia nitrogen shown in Column 7 was synthesized into cell protoplasm of the nitrifiers and saprophytes. It is felt that this was a valid assumption because the other common chemosynthetic and photosynthetic autotrophs generally need to oxidize reduced sulfur compounds ( $\text{H}_2\text{S}$ ),  $\text{H}_2$  or reduced carbon compounds ( $\text{CH}_4$ ,  $\text{CO}$ ), yielding energy for the assimilation of



TABLE 11  
CORRELATION BETWEEN NITRIFICATION AND OXYGEN UPTAKE IN 30-INCH FILTER DURING RUN 16

Time, hr	Nitrogen, mg/l						
	Ammonia-N (Influent Average)	NO <sub>2</sub> -N Formed (observed)	NO <sub>3</sub> -N Formed (observed)	Ammonia-N Oxidized (computed)	Ammonia-N Unoxidized (computed)	Ammonia-N in Effluent (observed)	Ammonia-N Synthesized as cell matter (7)=(5)-(6)
	(1)	(2)	(3)	(4)=(2)+(3)	(5)=(1)-(4)	(6)	(7)=(5)-(6)
2	2.95	0.09	0.44	0.53	2.42	1.92	1.50
8	2.95	0.29	0.88	1.17	1.78	0.98	0.80
16	2.95	0.35	1.01	1.36	1.59	0.71	0.88
24	2.95	0.20	1.08	1.28	1.67	0.44	1.23
32	2.95	nil	1.21	1.21	1.74	0.14	1.60
40	2.95	nil	1.23	1.23	1.72	nil	1.72
48	2.95	nil	1.26	1.26	1.69	nil	1.69

Time, hr	Dissolved Oxygen, mg/l				
	Influent (Average)	For NO <sub>2</sub> (computed)	For NO <sub>3</sub> (computed)	Total Demand (computed)	Remaining (computed)
	(8)	(9)	(10)	(11)=(9)+(10)	(12)=(8)-(11)
2	7.0	0.31	2.00	2.31	4.69
8	7.0	0.99	4.00	4.99	2.01
16	7.0	1.20	4.60	5.80	1.20
24	7.0	0.68	4.90	5.58	1.42
32	7.0	nil	5.50	5.50	1.50
40	7.0	nil	5.60	5.60	1.40
48	7.0	nil	5.72	5.72	1.28

Column 7: The values represent the fraction of ammonia nitrogen that was probably synthesized into the bacterial cell mass.

Column 9: The values were computed using Equation 1, Table 3.

Column 10: The values were computed using Equation 3, Table 3.

Column 14: The values represent the amount of dissolved oxygen that was probably used for deriving energy for the species of aerobic bacteria other than the nitrifiers.



inorganic carbon (98). Except for negligible amounts of  $\text{CH}_4$  these compounds were absent in the natural raw water at Clinton.

By subtracting the observed residual values of DO at a given time from the computed ones, it was possible to determine the amount of DO utilized by the species of aerobes other than the nitrifiers for the energy-yielding oxidation processes. These results are shown in Column 14. This value was fairly constant during the filtration period. From these computations, it can be seen that a good correlation existed among the amount of ammonia oxidized, the amount of DO depleted and the amount of oxidized nitrogen compounds found in the effluent at any given time.

#### 4.2.1.4 Effect of Nitrification on the pH and Alkalinity

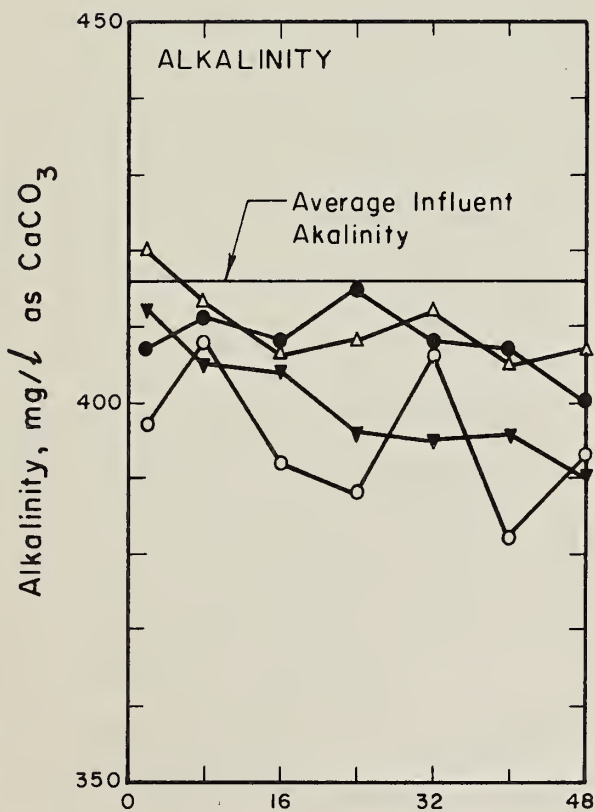
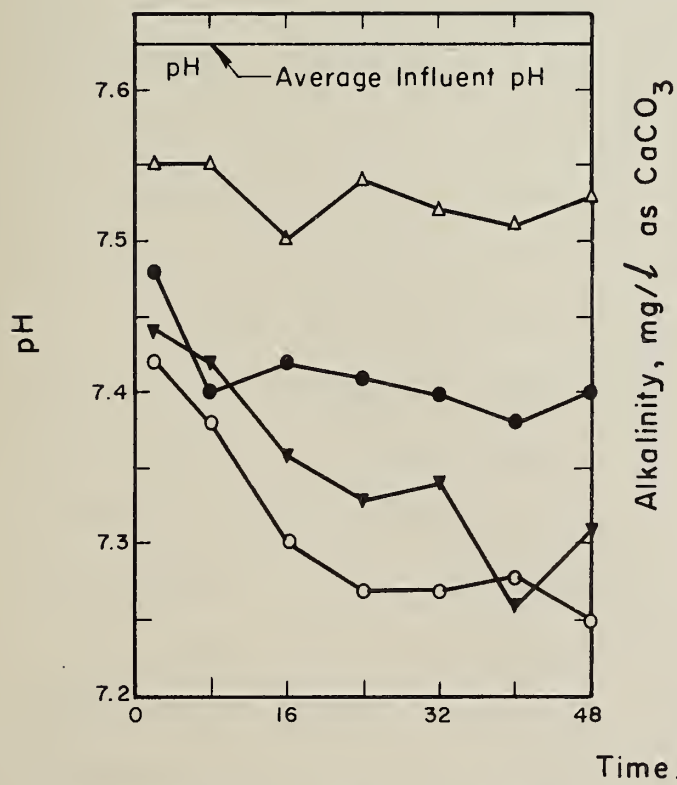
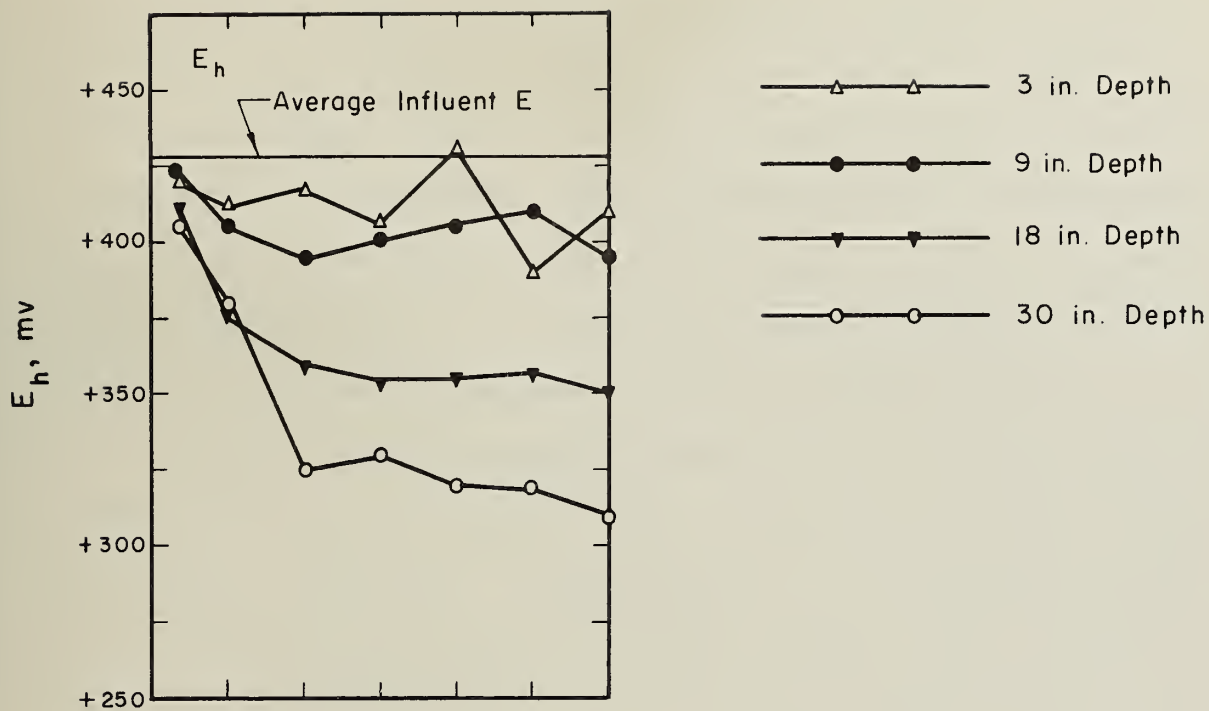
An important aspect of microbial nitrification which could play a significant role in changing the chemical environment within a filter is the production of  $\text{H}^+$  ions as illustrated by Equations 1 and 3 in Table 3. Larson (88) made a similar observation in his investigation on biologically mediated corrosion of iron. Such acid-producing reactions could lead to a decrease in pH and alkalinity resulting in the solution of precipitated ferrous iron or the desorption of any adsorbed ferrous iron.

Figure 29 shows the pH,  $E_h$  and alkalinity values for the filter effluent during Run 16. No appreciable change in pH and alkalinity values was observed in the 3-inch filter. There was no significant nitrification in this filter. However, in the 18- and 30-inch filters there was an appreciable decrease in the pH and alkalinity. The 9-inch filter also exhibited some decrease in these values.

There was no appreciable change in the  $E_h$  value of the effluent as compared to the influent from the 3- and 9-inch filters. However, the



Run 16

FIGURE 29. pH,  $E_h$  AND ALKALINITY OF FILTER EFFLUENT



18- and 30-inch filters exhibited an appreciable decrease in  $E_h$  during the course of the filtration period. The total depletion of oxygen in these filters (Figure 28) was associated with the decrease in  $E_h$ . This created a reducing environment in the filter which resulted in the reduction of iron from the ferric to the ferrous state at depths of 18 inches or more. However, there was a discrepancy between the observed and computed  $E_h$  values. This is discussed in detail in Section 4.2.1.5.

Table 12 shows the degree of reduction of the pH and alkalinity of the water due to nitrification. Only the data for the 30-inch filter are included in the table. The computation of  $H^+$  ion produced is based on the estimated values of ammonia nitrogen oxidized, shown in Column 4, Table 11. Compared with the  $H^+$  ion produced due to nitrification, the initial  $H^+$  ion content of the influent is insignificant. Hence, it was neglected in computing the expected pH from the indicated degree of nitrification. The computed pH values shown in Column 3 indicate that had it not been for the natural buffer present in the water, the pH value would have decreased to 3.74 after 48 hours. The actual decrease in pH was, however, much less than that predicted theoretically.

The production of  $H^+$  ion resulted in a decrease in alkalinity which is shown in Column 6. The observed decreases in alkalinity were much less than the computed values. This may be attributed to the precipitation of hardness-producing cations and the inorganic carbon uptake from  $HCO_3^-$  and  $CO_3^{=}$  by the nitrifying bacteria or other autotrophs.

The decrease in pH would increase the solubility of the sparingly soluble salts of ferrous iron, e.g.,  $FeCO_3$ ,  $Fe(OH)_2$ . The increase in the concentration of soluble ferrous iron in the effluent from the 18- and 30-inch filters (Figure 23) was made possible by the decrease in pH. However,



TABLE 12

EFFECT OF NITRIFICATION ON pH AND ALKALINITY OF WATER IN THE 30-INCH FILTER DURING RUN 16

Time, hr	H <sup>+</sup> ion Produced x 10 <sup>5</sup> , mol/l (1)	pH		Alkalinity (HCO <sub>3</sub> <sup>-</sup> ) as mg/l CaCO <sub>3</sub>					
		Influent (observed) (2)	Effluent (computed) (3)	Effluent (observed) (4)	Influent (observed) (5)	Reduction (computed) (6)	Remaining (computed) (7)=(5)-(6)	Effluent (observed) (8)	Balance (computed) (9)=(7)-(8)
2	7.6	7.58	4.12	7.42	408	3.8	404.2	397	11
8	16.7	7.68	3.79	7.38	425	8.9	416.1	408	17
16	19.4	7.62	3.71	7.30	415	9.7	405.3	392	23
24	18.3	7.57	3.74	7.27	408	9.2	398.8	388	20
32	17.3	7.61	3.76	7.27	435	8.7	426.3	406	29
40	17.6	7.67	3.75	7.28	410	8.8	401.2	382	28
48	18.0	7.66	3.74	7.25	415	9.0	406.0	393	22

Column 1: The values were computed from the data of total ammonia nitrogen oxidized (Column 4, Table 11) using Equations 1 and 2, Table 3.

Column 3: The values were computed from H<sup>+</sup> ion concentrations in Column 1 and represent the pH of effluent had there been no alkalinity present.

Column 5: The total alkalinity of the influent was primarily in bicarbonate form as calculated using the method given by Fair and Geyer (34).

Column 6: The values were computed from H<sup>+</sup> ion concentration (Column 1) using Equations 1 and 2, Table 3.

Column 9: The values represent the alkalinity reduction perhaps due to the bacterial uptake of inorganic carbon (nitrifiers) or precipitation of hardness.



the solubility of ferrous iron computed from Figures 1 and 2 at the observed pH of the effluent is much less than the observed concentrations of the soluble ferrous iron in the effluents from the 18- and 30-inch filters. This may have been due to the formation of some soluble ferrous iron complexes which were not considered in the computations for the solubility of iron.

#### 4.2.1.5 Evaluation of the Observed $E_h$ Values

Only the  $E_h$  data for the effluent from the 30-inch filter during Run 16 are considered in this discussion. The redox couples that may be operative within a filter under the observed conditions are listed in Table 13. The molar concentrations of the pertinent oxidative and reductive components ( $\text{NH}_4^+$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{Fe}^{++}$ ,  $\text{O}_2$ ) were computed from the observed values. These concentrations were used in computing the  $E_h$  for the independent half-cell reactions for the couples shown in Columns 1 through 5.

Solid-phase reduction of iron occurs only at negative potentials which are rarely achieved in natural waters. The observed  $E_h$  values differed widely from the  $E_h$  of any single couple shown in the table. Many redox reactants encountered in natural waters behave irreversibly at inert electrodes. Most organic redox couples behave irreversibly (31). The organic couples that may have existed under conditions of the present study were not known. The heterogeneity of the system made it impossible to ascertain the contribution of each pertinent couple to the overall  $E_h$  of the water. Therefore, it may be said that the  $E_h$  values observed in this study represented only mixed potentials. The net chemical reaction that occurred at the electrode was not representative of any single half reaction considered in the table.



TABLE 13

EVALUATION OF OBSERVED  $E_h$  VALUES FOR 30-INCH DEEP FILTER DURING RUN 16

Time, hr	Iron, Molar $\times 10^6$			Nitrogenous Com- ponents, Molar			DO, Molar $\times 10^4$	pH	Computed Independent Couple $E_h$ , mv					Observed $E_h$ , mv				
	Ferric	Soluble Ferrous	Insoluble Ferrous	$\text{NH}_4^+$ $\times 10^5$	$\text{NO}_2^-$ $\times 10^5$	$\text{NO}_3^-$ $\times 10^5$												
									$\text{NH}_4^+$	$\text{NO}_2^-$	$\text{NO}_3^-$	$\text{NH}_4^+$	$\text{NO}_2^-$		$\text{NO}_3^-$	$\text{Fe(OH)}_3^-$	$\text{Fe(OH)}_2$	$\text{Fe}^{++}$
(1)	(2)	(3)	(4)	(5)														
2	0.54	1.79	nil	12.90	0.72	3.15	1.06	7.42	+860	+887	+915	-169	+80	+405				
8	0.36	1.44	0.89	6.60	2.06	6.30	0.38	7.38	+882	+899	+855	-166	+115	+380				
16	1.79	1.79	1.44	4.76	2.50	7.21	0.16	7.30	+884	+897	+854	-163	+104	+325				
24	2.47	3.25	8.65	2.95	1.43	7.74	0.06	7.27	+886	+896	+860	-159	+98	+330				
32	4.50	5.03	7.55	0.95	nil	8.70	nil	7.27	+892			-159	+87	+320				
40	3.06	8.65	6.30	0.06	nil	8.80	nil	7.28	+904			-160	+68	+317				
48	3.58	8.65	6.67	nil	nil	9.00	nil	7.25				-158	+73	+310				

Column 1: Computed from Equation 3, Table 3 (oxidation)

Column 2: Computed from Equation 9, Table 3 (oxidation)

Column 3: Computed from Equation 11, Table 3 (oxidation)

Column 4: Computed from Equation 12, Table 2 (reduction)

Column 5: Computed from Equation 10, Table 2 (reduction)



It is believed that the nitrite that is formed in the first stage of nitrification of ammonia may have reduced ferric iron, the nitrite being oxidized, in the process, to nitrate. In order for ferric iron to oxidize nitrite, the  $E_h$  value for its oxidation must be higher than that for the nitrite oxidation. Equations 12a and 12b, Table 3, indicate that this is not possible. However, in the laboratory, studies were made to investigate the possibility of reducing ferric iron with nitrite. Upon the addition of sodium nitrite to ferric chloride solutions, stoichiometrically, there was evidence that ferrous iron was formed. Figure 28 shows that the nitrite concentration in the effluent from the 18- and 30-inch filters gradually decreased with a resulting increase in the nitrate concentration. It appears that nitrite was oxidized by ferric iron. The reduction of ferric iron was initiated at approximately the same time that the nitrite concentration began to decrease. Such was not the case in the 3- and 9-inch filters which exhibited no reduction of iron from the ferric to the ferrous form.

In the opinion of the author, the observed  $E_h$  values in natural waters are not indicative of the actual thermodynamic state of the system. Therefore, it is rather difficult to predict the chemical behavior of a natural water from its measured  $E_h$  values.

#### 4.2.1.6 Fate of Iron in the 30-inch Filter

In the preceding sections an attempt has been made to explain the mechanism by which iron may be reduced from the ferric to the ferrous form and also the mechanism by which the insoluble ferrous iron may be put back into solution. In this section the fate of iron during filtration will be discussed in the light of the aforementioned mechanisms.



Table 14 shows the concentration of the different forms of iron in the effluent from the 30-inch filter during Run 16. The ratios between the different forms of iron were computed from the observed concentrations. The table also indicates the DO, pH and  $E_h$  values at different times during filtration. An average composition of the influent water is given at the bottom of the table.

The effect of DO depletion and decrease in pH is apparent from a comparison between Columns 1, 2, 3 and 4 with the corresponding values in the influent.

The effect of the decrease in  $E_h$  and depletion of DO would be expected to result in an increase in the total ferrous to ferric iron ratio shown in Column 5 due to the reduction of iron from the ferric to the ferrous state. Except for the values at the initial stages of the filtration period, the observed results were generally in agreement with this hypothesis.

As the  $E_h$  decreased, the insoluble ferrous to ferric iron ratio shown in Column 6 would tend to increase due to the increase in the insoluble ferrous iron caused by the reduction of iron from the ferric to the ferrous state. However, the actual values were not in agreement with the hypothesis. This was probably due to the fact that the observed decrease in the pH resulted in a conversion of insoluble ferrous iron to the soluble ferrous form. Hence, the observed values of the insoluble ferrous iron would be lowered.

As the pH decreased, the ratio of total ferrous to soluble ferrous iron shown in Column 7 might be expected to decrease due to an increase in the soluble ferrous iron fraction. The actual values did not show this result. Because of the reduction of iron from the ferric to the ferrous



TABLE 14  
FATE OF IRON IN THE 30-INCH FILTER DURING RUN 16

Time, hr	Iron, mg/l				Total		Insoluble		DO, mg/l	pH	E <sub>h</sub> , mv
	Ferric (1)	Total Ferrous (2)	Soluble Ferrous (3)	Insoluble Ferrous (4)=(2)-(3)	Ferric (5)=(2)/(1)	Ferrous: Ferric (6)=(4)/(1)	Ferrous: Soluble Ferrous (7)=(2)/(3)	Ferrous: Soluble Ferrous (8)=(4)/(3)			
2	0.03	0.10	0.10	nil	3.33	--	1.00	--	3.4	7.42	+405
8	0.02	0.13	0.08	0.05	6.50	2.50	1.62	0.63	1.2	7.38	+380
16	0.10	0.18	0.10	0.08	1.80	0.80	1.80	0.80	0.5	7.30	+325
24	0.14	0.56	0.18	0.48	4.00	3.42	3.11	2.66	0.2	7.27	+330
32	0.25	0.60	0.28	0.42	2.40	1.68	2.15	1.50	nil	7.27	+320
40	0.17	0.83	0.48	0.35	4.85	2.05	1.72	0.73	nil	7.28	+317
48	0.20	0.85	0.48	0.37	4.25	1.85	1.90	0.77	nil	7.25	+310
Average Influent Composition											
Ferric Iron											
Total Ferrous Iron											
Soluble Ferrous Iron											
Insoluble Ferrous Iron											
Total Ferrous:Ferric											
Insoluble Ferrous:Ferric											
Total Ferrous:Soluble Ferrous											
Insoluble Ferrous:Soluble Ferrous											
DO											
pH											
E <sub>h</sub>											

1.19 mg/l  
0.45 mg/l  
0.08 mg/l  
0.37 mg/l  
0.38  
0.31  
5.62  
4.14  
7 mg/l  
7.63  
+428 mv



state, the total ferrous iron concentration gradually increased. This influence, added to the increase in soluble ferrous iron, led to fluctuations in the total-soluble ferrous iron ratio.

As the pH decreased the ratio of insoluble ferrous to soluble ferrous iron shown in Column 8 would be expected to decrease. The observed ratios were in agreement with this hypothesis except during the initial stages of filtration where both insoluble ferrous and soluble ferrous iron concentrations were close to the limit of analytical detection.

#### 4.2.1.7 Biological Growth during Filtration

The concentration of COD and organic nitrogen in the effluent from the filters during Run 16 is shown in Figure 30. Figure 31 shows the bacterial count in the effluent samples from the filters.

The COD and organic nitrogen contents of the effluent were generally less than that of the influent. This indicated that most of the bacteria were being retained in the filter. No appreciable amounts of COD or organic nitrogen were found in the supernatant of centrifuged effluent samples. However, as indicated earlier, the influent contained appreciable amounts of COD and organic nitrogen in solution. Therefore, it appears that the soluble COD and organic nitrogen were being utilized for bacterial growth.

The COD and organic nitrogen being passed by the filters increased with an increase in time of filtration. This was due to the fact that the filters were passing an increasing number of bacteria as they became clogged. At any given time, the amount of COD, organic nitrogen and the number of bacteria being passed by a filter generally depended on filter depth. The deeper filters passed smaller amounts of COD, organic nitrogen, and bacteria.



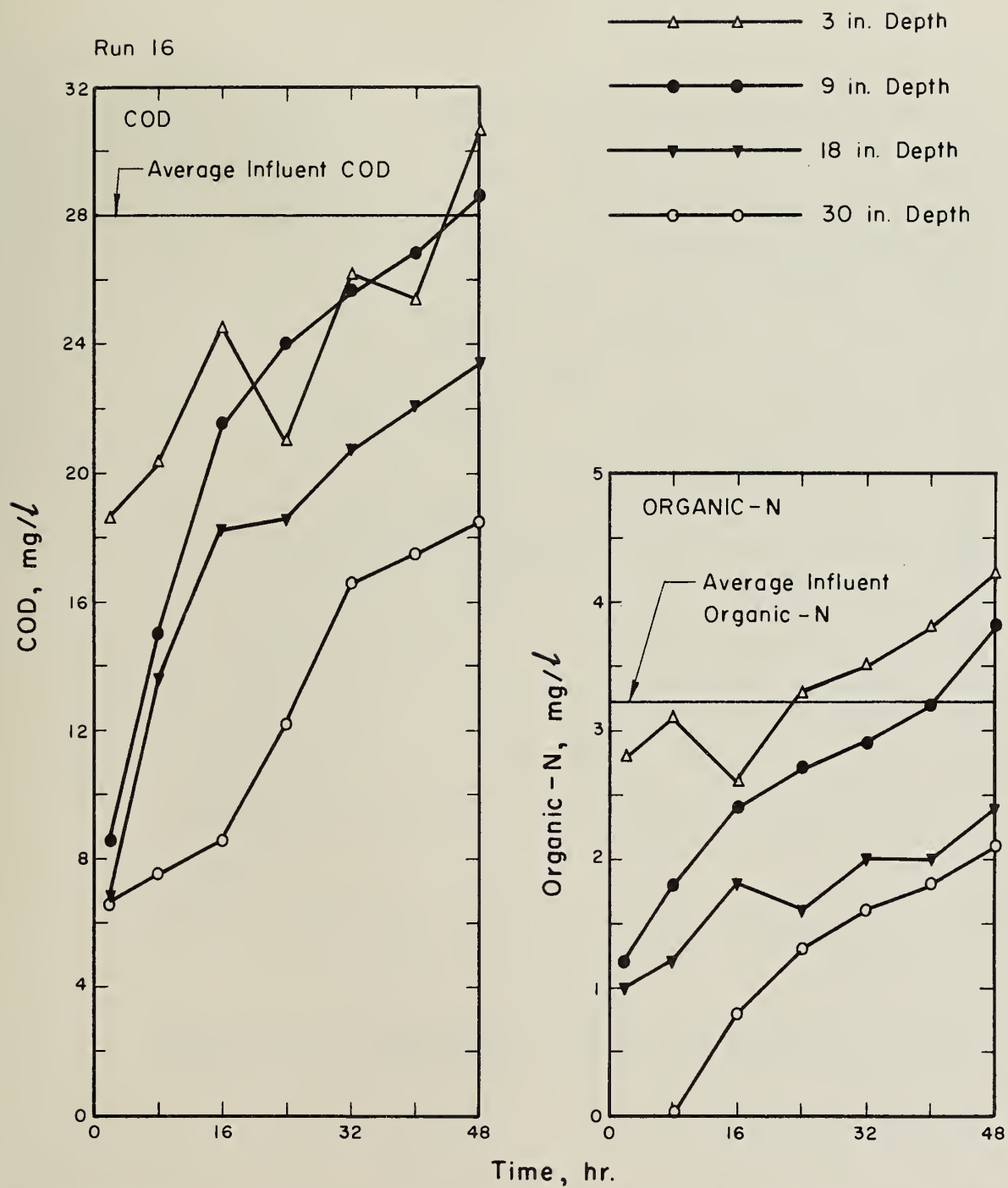


FIGURE 30. COD AND ORGANIC NITROGEN IN FILTER EFFLUENT



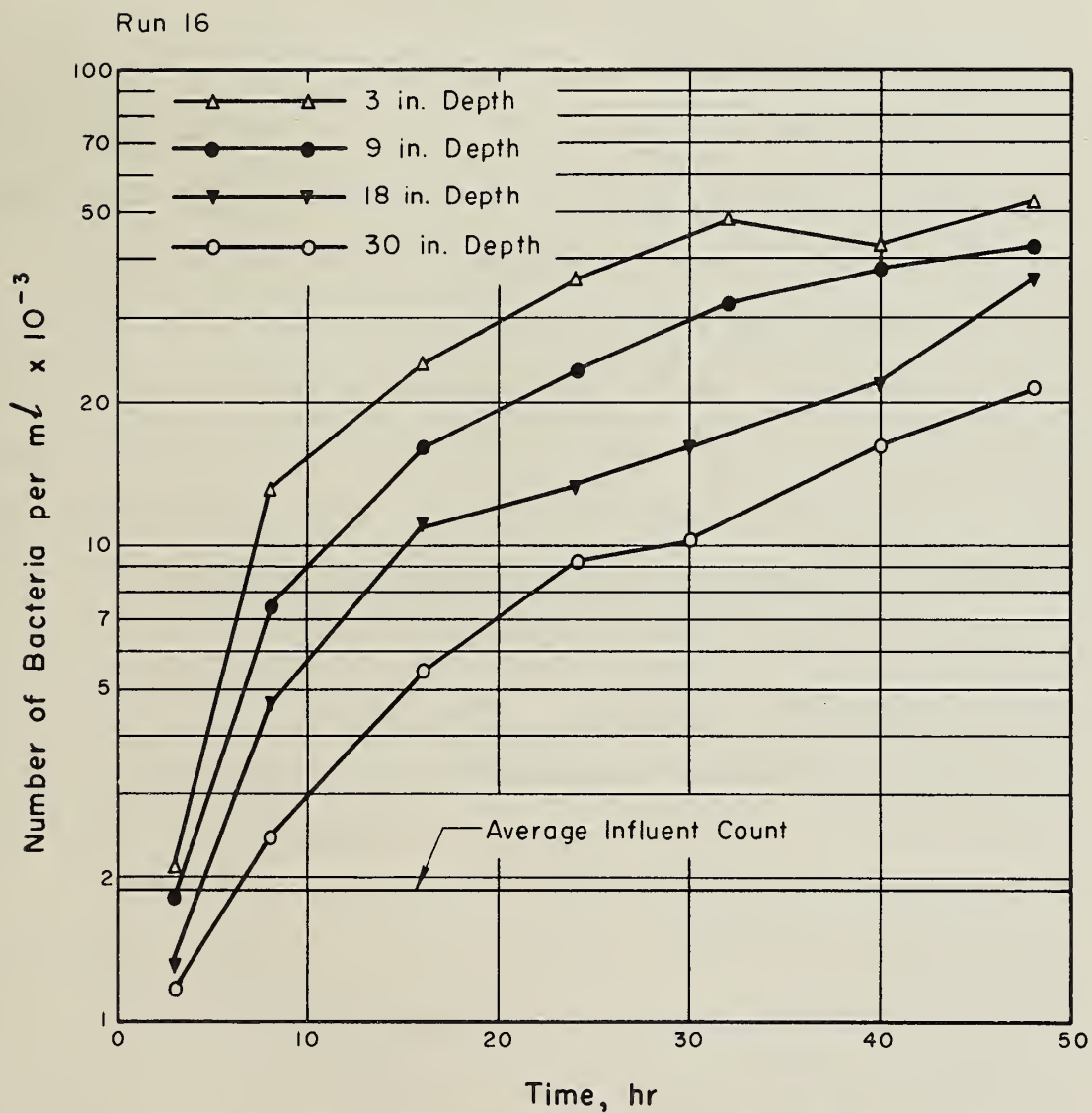


FIGURE 31. BACTERIAL COUNT IN THE EFFLUENT



It appeared from Figure 31 that there was a limiting bacterial population that could be retained on a filter of a given depth.

Table 15 shows a relationship between the organic carbon and organic nitrogen contents in the effluent from the 30-inch filter during Run 16. The ratio varied between 3.12 to 4.03. This is approximately the C:N ratio found in bacterial cells. This further indicates that all the COD and organic nitrogen in the effluent were present in the cell mass.

An analysis of the sand samples at various depths for Run 21 is shown in Table 16. The data were collected at the conclusion of Run 21 which was the last filter run performed during 1964. The data show that in deeper sections of a 30-inch filter, a large fraction of the precipitated iron was in the ferrous form. The ferrous iron may have been in the insoluble state or adsorbed on the ferric hydrates. The percent of ferrous iron in the precipitate was found to vary from 10 percent near the surface of the filter to 30 percent at the bottom. The organic nitrogen and COD data followed the same trend as the bacterial count. These three values were highest at the filter surface.

#### 4.3 Inhibition Studies

From the preceding discussions it is apparent that the ripened filters at Clinton showed evidence of nitrification. Efforts were made to inhibit the bacterial growth and maintain aerobic conditions in the filter.

Runs 22 and 27 were made during the summer of 1965 using two 30-inch filters. One of the filters, referred to as the "control" hereafter, was fed a dose of the inhibitor continuously from the beginning of operation. However, the other 30-inch filter was allowed to ripen before the inhibitor was used. Runs 22 and 27 were made only after ripening conditions had



TABLE 15

ORGANIC CARBON TO ORGANIC NITROGEN RATIO IN THE  
EFFLUENT AT 30-INCH DEPTH DURING RUN 16

Time, hr	COD, mg/l	Organic-C,* mg/l	Organic-N mg/l	C:N (by wt.)
2	6.6	2.48	nil	NA
8	7.5	2.81	nil	NA
16	8.6	3.22	0.8	4.03
24	12.2	4.06	1.3	3.12
32	16.6	6.22	1.6	3.90
40	17.5	6.68	1.8	3.70
48	18.5	6.92	2.1	3.30

\*Assuming that the COD data can be used to estimate the  $O_2$  needed for the combustion of the total organic carbon present in the sample, the organic carbon content can be calculated from the following reaction:

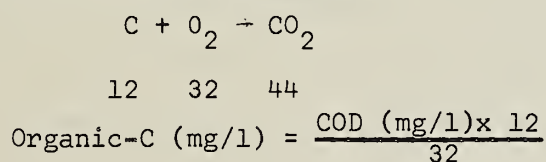


TABLE 16

SAND ANALYSIS AT THE CONCLUSION OF RUN 21

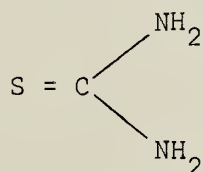
Depth, in	Iron, mg/gm of sand		Percent Ferrous	COD, mg/gm of sand	Organic-N, mg/gm of sand	Bacterial Count, mo./mg of sand
	Total	Total Ferrous				
0.25	37.8	3.9	10.3	182.0	18.7	380,000
3	23.2	2.5	10.6	65.0	6.4	93,000
9	16.7	2.6	15.4	18.5	1.8	12,500
18	14.6	3.7	25.5	8.3	0.6	3,800
30	12.3	3.6	28.9	4.5	0.4	2,400



developed in the filter where no inhibitor was used.

#### 4.3.1 Inhibition of Nitrosomonas with Thiourea

Thiourea is an inhibitor specific for the growth of the nitrite-forming organism, Nitrosomonas. It has the structure,



and a molecular weight of 76. For the purposes of this study three dosages were used, namely,  $10^{-5}$ ,  $5 \times 10^{-5}$  and  $10^{-4}$  molar in three filter runs. With a dosage of  $10^{-4}$  M, nitrification never occurred in the control filter. Furthermore, nitrification could be eliminated in the ripened filters after 24 hours of continuous feeding of thiourea at a rate of 7.6 mg/l ( $10^{-4}$  M).

Table 17 shows the average influent composition of the water during Run 24 when thiourea was fed at a rate of 7.6 mg/l ( $10^{-4}$  M) to both the filters. The concentration of iron being passed by the ripened filter prior to the addition of thiourea is shown in Figure 32 for Run 22. The same figure also shows the effluent iron concentrations from the control and the ripened filter during Run 24. Run 24 was made following the addition of thiourea for 24 hours to the ripened filter. Comparing the control and ripened filter during Run 24, it is apparent that both filters performed with equal efficiency. There was no reduction of ferric iron to the ferrous form and no appreciable increase in the soluble ferrous iron content in the effluent from either of the filters during this run.

Table 18 shows the quality of the effluent from both the control



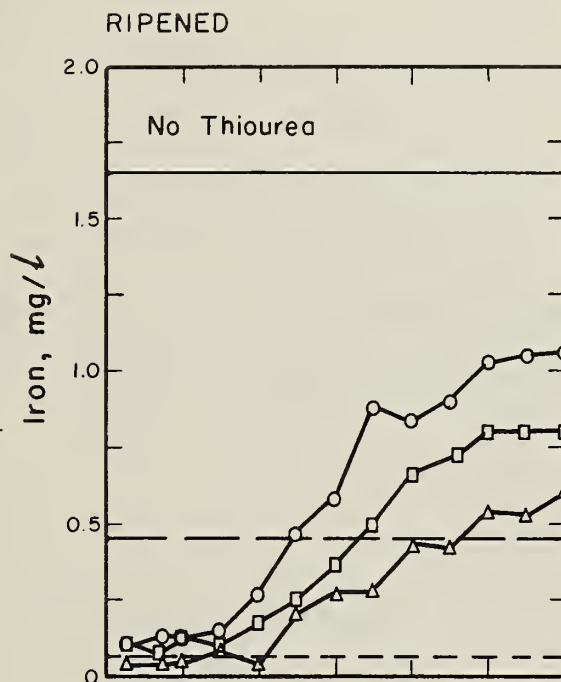
Run 22

—○—○— Total Fe  
 —□—□— Total Fe<sup>++</sup>  
 —△—△— Soluble Fe<sup>++</sup>

— Average Influent Total Fe

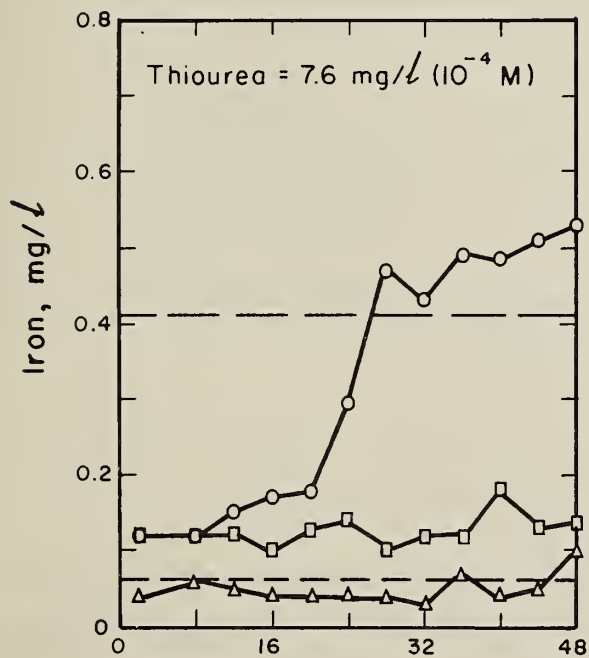
— Average Influent Total Fe<sup>++</sup>

--- Average Influent Soluble Fe<sup>++</sup>



Run 24

CONTROL



RIPENED

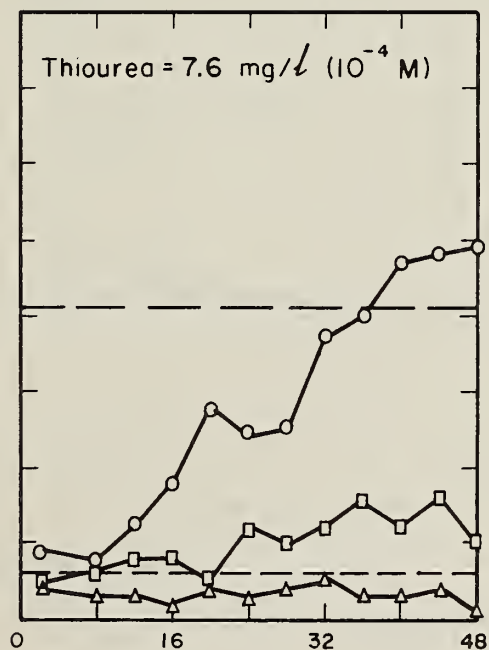


FIGURE 32. IMPROVEMENT OF IRON REMOVAL EFFICIENCY WITH THIOUREA



and the ripened filter during Run 24. The data indicate that no nitrification occurred in either of the filters. The slight increase in the organic nitrogen content (influent organic nitrogen = 3.2 mg/l) toward the end of the run was perhaps due to the contribution of organic nitrogen by the addition of thiourea. The bacterial count in the effluent was rather high. This suggests that thiourea was ineffective in inhibiting the growth of bacterial species other than Nitrosomonas. Sufficient DO was carried through the filters. The pH and  $E_h$  values of the water did not change significantly during the run.

TABLE 17  
AVERAGE COMPOSITION OF INFLUENT WATER DURING RUN 24

Total Iron	1.68 mg/l
Total Ferrous Iron	0.41 mg/l
Soluble Ferrous Iron	0.06 mg/l
Dissolved Oxygen	7.3 mg/l
pH	7.70
$E_h$	+438 mv
Alkalinity	428 mg/l as $\text{CaCO}_3$
Ammonia Nitrogen	2.90 mg/l
Organic Nitrogen	3.2 mg/l
Nitrite Nitrogen	nil
Nitrate Nitrogen	nil
COD	28.3 mg/l
Bacterial Count	1,800 per ml

#### 4.3.2 Inhibition of Bacterial Growth with "Roccal"

Following Run 24, both filters were fed 10 percent solution of "Roccal" at the rate of 5 ml/l. This was done in an effort to control bacterial growth completely since "Roccal" is a general inhibitor for most species of bacteria.

The results from a typical filter run, Run 27, when "Roccal" was







being fed continuously, are discussed below. Table 19 shows the average composition of the influent during Run 27. Figure 33 shows the effluent iron concentration in the control and the ripened filter. The results were very similar to that of Run 24. Again, there was no evidence of reduction of the ferric iron to the ferrous form or increase in the soluble ferrous iron concentration.

Table 20 shows the chemical characteristics of the effluent from the control and the ripened filter. It was possible to carry DO through the filters throughout the filtration period. The change in  $E_h$  and pH were insignificant. As expected, the bacterial count in the effluent from both filters was quite low.

The inhibition studies indicated that by maintaining aerobic conditions in the filters through the use of thiourea or "Roccal," not only

TABLE 19  
AVERAGE COMPOSITION OF INFLUENT WATER DURING RUN 27

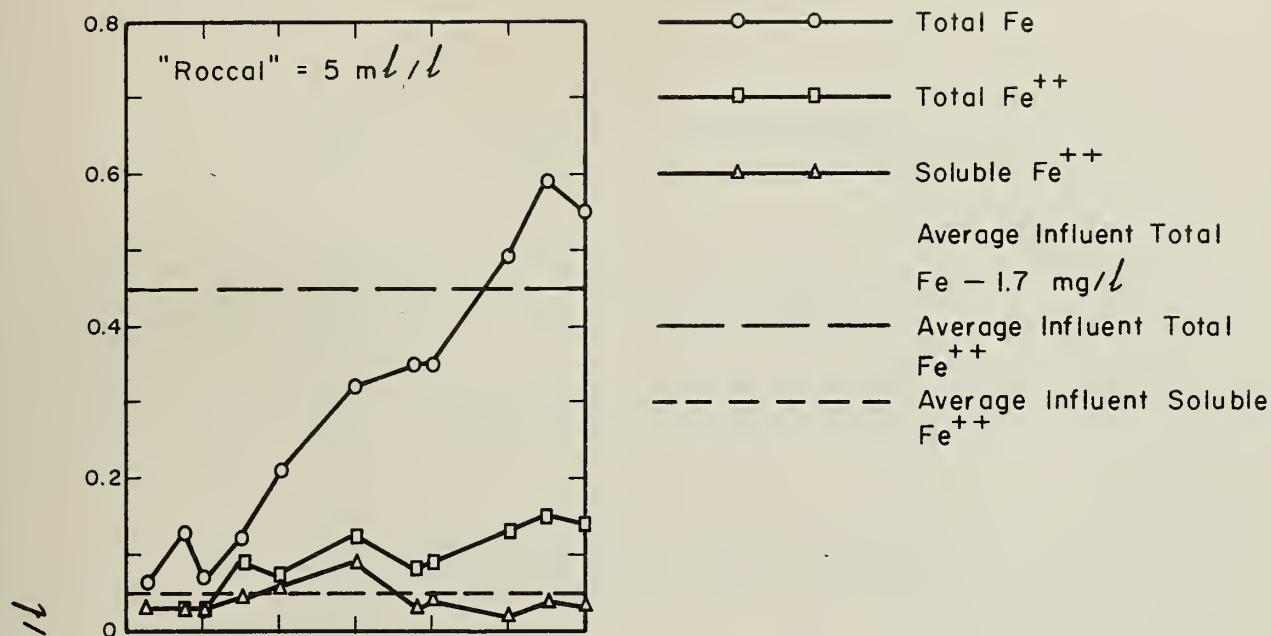
Total Iron	1.7 mg/l
Total Ferrous Iron	0.45 mg/l
Soluble Ferrous Iron	0.05 mg/l
Dissolved Oxygen	7.5 mg/l
pH	7.65
$E_h$	+426 mv
Alkalinity	432 mg/l as $\text{CaCO}_3$
Ammonia Nitrogen	3.1 mg/l
Organic Nitrogen	2.7 mg/l
Nitrite Nitrogen	nil
Nitrate Nitrogen	nil
COD	30.2 mg/l
Bacterial Count	2,500 per ml

was it possible to stop reduction of iron but also a considerable fraction of the influent ferrous iron was oxidized within the filters. Therefore, nitrification appears to be the prime cause of problems associated with



Run 27

RIPENED



CONTROL

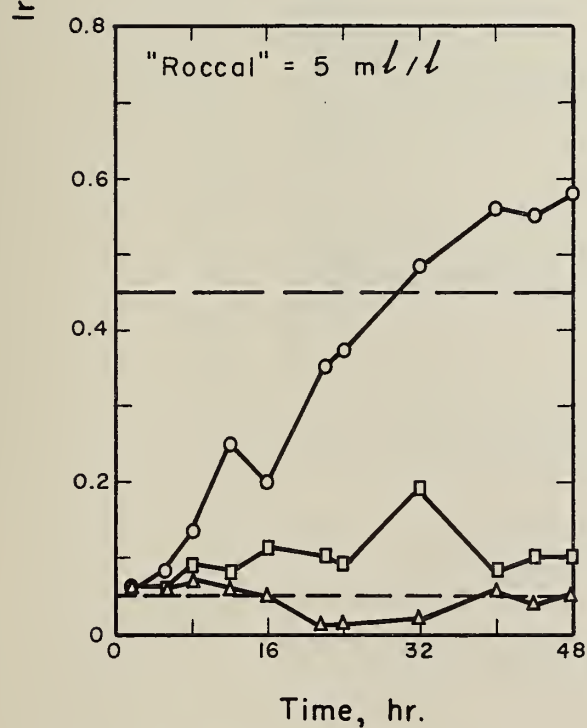


FIGURE 33. IMPROVEMENT OF IRON REMOVAL EFFICIENCY WITH "ROCCAL"







the removal of iron from waters containing ammonia.

#### 4.4 Chlorination Studies

In an effort to find an economical and practical remedial measure to improve the conditions in a ripened filter, preliminary investigations were carried out with chlorination of the influent prior to filtration. Once again the investigation was carried out on two 30-inch filters, one of which was used as a control.

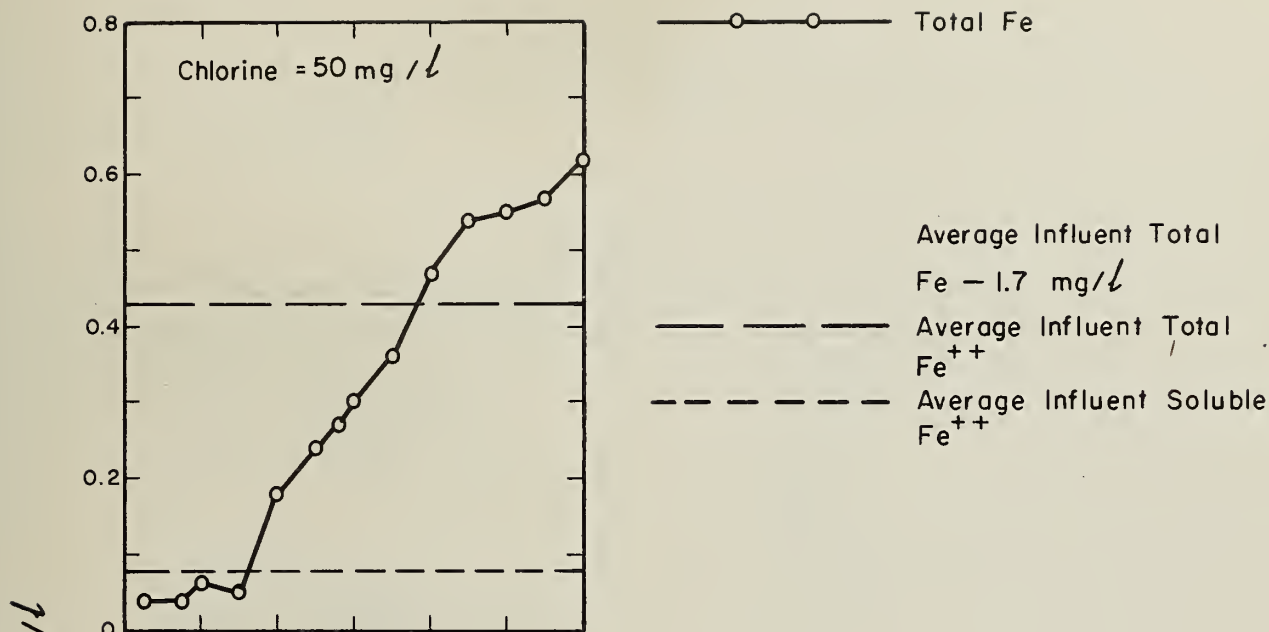
One of the filters was allowed to ripen. When reducing conditions developed in the ripened filters, chlorination was initiated. The control in this case was a new filter which was not placed in service until reducing conditions were evident in the ripened filter. Three filter runs, Runs 28 through 30, were made using chlorine. The dosages used for both control and the ripened filter were 5 mg/l (Run 28), 8 mg/l (Run 29) and 50 mg/l (Run 30). It was observed that a chlorine residual of 0.2 mg/l could be maintained in the control at a dosage of 8 mg/l. However, at this dosage no residual could be maintained in the ripened filter. Furthermore, nitrification could not be completely inhibited in either of the filters at a chlorine dosage of 5 or 8 mg/l. This was due to the fact that at these dosages the ammonia present in the water could not be completely destroyed, which was confirmed by the presence of ammonia in the effluent. Therefore, superchlorination with a dosage of 50 mg/l was undertaken to destroy all the ammonia present in order to inhibit the energy-yielding reactions in the growth of Nitrosomonas.

The results for Run 30 are discussed in this section. Table 21 shows the average influent composition during this filter run. Figure 34 shows the effluent iron concentration during the run. There was no ferrous



Run 30

RIPENED



CONTROL

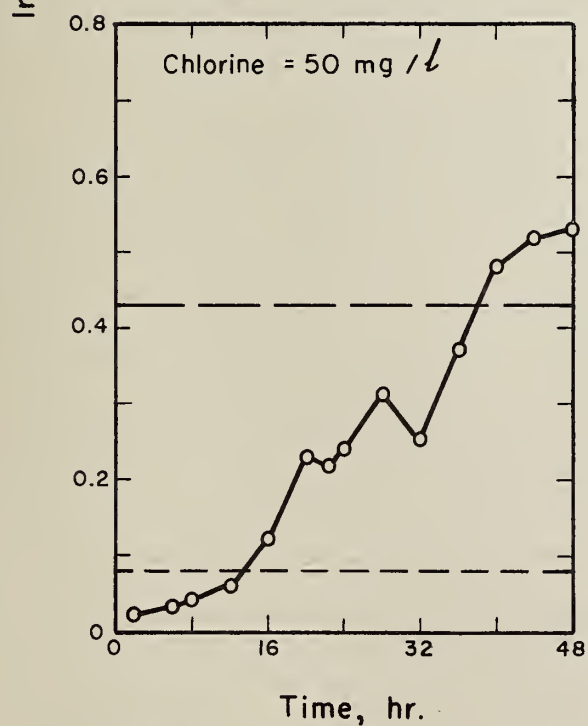


FIGURE 34. IMPROVEMENT OF IRON REMOVAL EFFICIENCY WITH CHLORINE



iron in the effluent from either of the filters at any given time during the filtration period. As chlorine is a very strong oxidant, having an oxidation potential higher than that of oxygen, no ferrous iron was to be expected in the effluent.

TABLE 21  
AVERAGE COMPOSITION OF INFLUENT WATER DURING RUN 30

Total Iron	1.65 mg/l
Total Ferrous Iron	0.43 mg/l
Soluble Ferrous Iron	0.08 mg/l
Dissolved Oxygen	7.2 mg/l
pH	7.62
ORP	+442 mv
Alkalinity	430 mg/l as $\text{CaCO}_3$
Ammonia Nitrogen	2.8 mg/l
Organic Nitrogen	3.3 mg/l
Nitrite Nitrogen	nil
Nitrate Nitrogen	nil
COD	32.5 mg/l
Bacterial Count	2,100 per ml

Table 22 shows the chemical characteristics of the effluent from the control and the ripened filter. There was no evidence of nitrification in the control. However, small amounts of nitrate were present in the ripened filter effluent. This indicates that the nitrifying organisms could not be inhibited altogether even at a dosage of 50 mg/l. Feben (87) reported that the nitrifying bacteria could withstand a chlorine dosage of 6 mg/l for a contact time of 60 minutes. Nevertheless, a chlorine residual could be carried through the ripened filter and thus it was possible to maintain an oxidizing environment within the filter. The bacterial count in the effluent was low as was the COD and the organic nitrogen. This was because chlorine oxidized most of the organic compounds present in the water. Therefore, it seems that some method should be devised to remove ammonia prior to filtration. Use of chlorine for destroying ammonia in the water is uneconomical.



TABLE 22

QUALITY OF FILTERED WATER DURING RUN 30 WITH CONTINUOUS CHLORINE FEED

Filter	Time, hr	Chlorine Residual, mg/l	pH	E <sub>h</sub> , mv	Alkalinity, mg/l as CaCO <sub>3</sub>	Nitrogen, mg/l			COD mg/l	Bacterial Count, no./ml
						Organic	Ammonia	Nitrite		
30-inch control	2	6.9	7.50	+452	418	nil	nil	nil	nil	160
	8	6.3	7.45	+463	415	nil	nil	nil	nil	84
	16	4.9	7.52	+458	415	nil	nil	nil	nil	140
	24	5.8	7.49	+466	428	nil	0.3	nil	1.7	93
	32	6.0	7.38	+440	410	0.8	nil	nil	2.1	9
	40	6.5	7.50	+437	406	nil	nil	nil	nil	63
	48	7.0	7.41	+454	419	nil	0.8	nil	nil	105
30-inch ripened	2	1.2	7.50	+457	416	nil	nil	nil	nil	230
	8	1.3	7.30	+455	402	nil	nil	nil	0.3	270
	16	0.7	7.42	+448	418	nil	nil	nil	0.1	73
	24	0.5	7.40	+440	422	nil	nil	nil	0.2	96
	32	1.0	7.40	+432	415	nil	nil	nil	0.1	55
	40	1.1	7.36	+450	420	nil	0.5	nil	0.2	120
	48	0.9	7.43	+458	416	nil	nil	nil	0.3	170



## 5. CONCLUSIONS

1. By aeration and settling it is possible to convert the soluble ferrous iron in the raw water to either the ferric form or an insoluble ferrous form, e.g.,  $\text{FeCO}_3$ ,  $\text{Fe(OH)}_2$ . Complete oxidation of the ferrous iron is not possible even with DO at the saturation level. It is, however, possible that a fraction of the ferrous iron may be adsorbed on the ferric hydrate precipitates.

2. It is not possible to settle all the insoluble iron at Clinton within a total reaction-sedimentation time of 48 minutes. Formation of stable sol particles of aqueous complexes of iron imparts poor flocculating characteristics to the insoluble iron. For satisfactory settling of such particles, destabilization of colloids by coagulation is needed.

3. Under normal conditions of operation when DO can be carried through the filter and there is no extensive biological growth in the filter, the removal of iron is quite satisfactory. The degree of removal depends on the depth of filtering medium. In addition, there is evidence of oxidation of ferrous iron within the filters. This may be due in part to a surface catalyzed reaction at the surface of sand grains coated with precipitated ferric oxide.

4. The changes in pH,  $E_h$  and DO during filtration are not significant under normal conditions of operation.

5. After a period of 8 to 10 weeks of continuous operation there is extensive biological growth in the filters. Dissolved oxygen is depleted during filtration especially at depths of 18 inches or more. There is also a significant decrease in pH and  $E_h$  at such depths. In addition, there is evidence of nitrification in the filters.



6. In ripened filters undergoing nitrification, iron is reduced from the ferric to the ferrous form at approximately the same time that the DO is depleted. At such times filters having depths of 18 inches or more pass large amounts of iron much of which is in the ferrous form. A large fraction of the ferrous iron being passed by the filters is in solution. The filter does not exhibit reducing conditions or a significant decrease in pH up to a depth of 9 inches. The dissolved oxygen is not totally depleted at this depth. Consequently, at this depth there is no reduction of iron from the ferric to the ferrous form. The iron passed in the effluent at the 9-inch depth is mostly in the ferric form. However, at a depth of 3 or 9 inches the filter passes considerable amounts of insoluble iron. Therefore, a filter depth of 9 inches seems to be insufficient for the effective removal of iron.

7. In a ripened filter the aerobic species of bacteria, especially the nitrifiers, predominate. With an increase in filtration time there is an increase in the bacterial population in the filters. Ultimately, the amount of DO in the influent falls short of the demand imposed by the growing aerobic population. This leads to a reducing condition in the deeper part of the filter. Such a phenomenon is accompanied by a decrease in the oxidation potential of the system. The creation of a reducing environment is then responsible for the reduction of iron from the ferric to the ferrous form. It appears that the nitrites formed as a result of the microbial nitrification of ammonia play an active role in the reduction of ferric iron.

Furthermore, nitrification involves the conversion of a cation ( $\text{NH}_4^+$ ) into an anion ( $\text{NO}_2^-$  or  $\text{NO}_3^-$ ) resulting in a release of  $\text{H}^+$  ions. This leads to a decrease in pH and alkalinity. Due to decreased pH in a



nitrifying filter there is an increase in the concentration of soluble ferrous iron passing out of the filter.

8. There is a good correlation between the amount of ammonia oxidized and the amount of DO depleted at any given time during filtration.

9. In the deeper sections of a ripened filter, the insoluble iron retained on the sand grains has a greater fraction of insoluble ferrous iron than that in the upper portions of the filter.

10. The number of bacteria passed by the filter depends on its depth. The smaller the depth, the larger the number of bacteria passed. Therefore, there seems to be a limiting bacterial population that can be supported by a filter of a certain depth.

11. The C:N ratio in the effluent ranges from 3.12 to 4.03. Also, there is negligible COD or organic nitrogen in the supernatant of the centrifuged effluent samples. This indicates that the COD and organic nitrogen in the effluent are contained in the bacterial cells being passed by the filter.

12. Nitrification in a filter can be effectively eliminated by using thiourea, an inhibitor specific for Nitrosomonas, at a rate of 7.6 mg/l ( $10^{-4}$  M). It is possible to restore a ripened filter to normal efficiency provided a continuous feed of the inhibitor is maintained. By inhibiting nitrification, it is possible to maintain aerobic conditions in a filter and thus prevent the reduction of iron from the ferric to the ferrous form.

13. The use of "Roccal," a general bacterial inhibitor, also makes it possible to maintain aerobic conditions in a filter by eliminating nitrification. The reduction of ferric iron is prevented using 5 ml/l of a 10 percent "Roccal" solution.



14. Preliminary investigations with prechlorination, chlorination of the influent to the filter, indicate that all bacterial growth can be effectively controlled in a ripened filter at a dosage of 50 mg/l of chlorine. A residual of approximately 1 mg/l can thereby be maintained through the filter. However, once a ripened filter is restored to normal operating condition, a lower dosage can be employed to maintain the same residual. Occasional superchlorination followed by a continuous feed of 8 mg/l is sufficient to maintain aerobic conditions in a ripened nitrifying filter at Clinton. Under such conditions it is also possible to oxidize all the ferrous iron in the filter.



## 6. PRACTICAL SIGNIFICANCE AND SCOPE OF FUTURE STUDY

### 6.1 Practical Significance

Most water treatment plants using ground waters containing iron practice some form of iron removal. The simplest method of removal and the one most widely used involves aeration, settling and rapid sand filtration. However, often proper consideration of the existing local conditions is not accounted for in the design of iron removal plants. Consequently, these plants do an unsatisfactory job of iron removal.

The practical significance of the current studies to the treatment plant operator and the design engineer is discussed below.

#### 6.1.1 Operation of an Iron Removal Plant

The most widely used index of iron removal efficiency is the total iron content in the filter effluent. Although it is indicative of the overall plant efficiency, this measurement alone is not a sufficient indication of the plant performance. A complete record of the different forms of iron (ferric, soluble ferrous and insoluble ferrous) and their concentrations at every stage of treatment should be maintained. The significance of these measurements has been discussed in the preceding chapters.

In order to achieve effective iron removal, it is essential that the filter be kept aerobic at all times. An unusual depletion of dissolved oxygen and a decrease in the pH and  $E_h$  values would indicate a malfunctioning of the filter. Therefore, these parameters should be monitored. It is not possible to relate the theoretically predicated  $E_h$  values to the observed values in a natural water. However, decreases from the observed normal  $E_h$  values may be taken as an indication of incipient failure of filtration.



In a filter exhibiting the characteristics of an anaerobic environment aerobic conditions may be restored by frequent backwashings, prechlorination with sufficient amounts of chlorine so that a residual is maintained in the effluent, the use of heavy dosages of chlorine during backwashes, or a combination of these techniques. Generally speaking, it is always advantageous to keep the bacterial population in a filter at a minimum level so that the depletion of dissolved oxygen remains insignificant.

#### 6.1.2 Design of New Iron Removal Plants

In designing an iron removal plant, it is necessary to determine the rate of oxidation of soluble ferrous iron to the ferric form. A still more important parameter that is often neglected in the design is the rate of precipitation of insoluble iron, both ferrous and ferric. It was demonstrated in the current study that effective removal of the insoluble iron could not be obtained by sedimentation. It is believed that the presence of naturally occurring organic compounds hinders settling of the insoluble iron by forming stable sols.

In alkaline waters, the formation of ferrous bicarbonate complexes may occur. This may retard oxidation and, consequently, the precipitation of iron. Ferrous iron may precipitate in such waters as  $\text{FeCO}_3 \cdot \text{Fe(OH)}_2$  or may be partially adsorbed on ferric oxide hydrates. Therefore, the determination of the proportion of ferrous and ferric iron in the iron precipitate from these waters is of concern to the designer.

To enhance oxidation of the ferrous iron, oxidizing agents, potassium permanganate and chlorine, for example, may be used as adjuncts to aeration. Furthermore, for effective sedimentation, the coagulation of



insoluble iron by suitable coagulating agents should be considered in the design.

The deleterious effects of the microbial oxidation of ammonia on the removal of iron by filtration have been demonstrated in the current research. The presence of other reduced compounds, methane and hydrogen sulfide, for example, may pose similar problems. On the other hand, reduced organic compounds, if present in the water, will support the growth of saprophytic bacteria in the filter. Therefore, all reduced compounds, both organic and inorganic, should be accounted for prior to design. Methods for the removal of these compounds prior to filtration should be considered in the design.

Provisions should be made in the design for prechlorination to guard against the development of anaerobic conditions in the filters. The plant should have a flexibility of operation which will ensure satisfactory performance and allow for the elimination of anaerobic conditions should they occur after the plant has been placed in service.

## 6.2 Scope of Future Work

On the basis of the results of the current study it is felt that further investigations should be pursued in the following areas.

a) Investigations involving the use of chlorine, potassium permanganate or other oxidizing agents as adjuncts to aeration should be made in an effort to achieve complete oxidation of ferrous iron prior to filtration.

b) Studies should be made to determine the factors that retard coagulation of insoluble iron. In short, methods should be developed to remove iron completely prior to filtration.



c) Preliminary investigations using chlorine at Clinton reveal that this oxidizing agent will maintain aerobic conditions in a filter. However, additional explorations under more varied conditions might give a better indication of the dosages of chlorine required and its effectiveness over prolonged periods of filtration.

d) Aerobic sand filters, or non-submerged dry filters as they are sometimes called, have been successfully employed in the Netherlands in removing iron from ground waters containing large amounts of ammonia nitrogen. The feasibility of maintaining aerobic conditions in such a filter should be explored.



## BIBLIOGRAPHY

1. Larson, T. E., "Mineral Content of Public Ground-Water Supplies in Illinois." State of Illinois, Department of Registration and Education, Illinois State Water Survey, Urbana, Illinois, Circ. 90, 4 (1963).
2. Public Health Service Drinking Water Standards, U.S.P.H.S. (1962).
3. Mohler, H., "Iron and Manganese as Disturbing Factors in Ground Water." Sweiz. Ver. Gas-U. Wasserfach Monats-Bull (Swiss), 31, 293 (1951), Abs. Jour. A.W.W.A., 44, 10 P and R 42 (1952).
4. Bell, G. R., "Removal of Soluble Iron by Filtration." Jour. A.W.W.A., 57, 4, 458 (1965).
5. Weston, R. S., "Some Recent Experiences in the Deferrization and Demanganization of Water." Jour. N.E.W.W.A., 28, 1, 27 (1914).
6. Weiss, J., "Elektronenübergangsprozesse im Mechanismus von Oxydation und Reduktionsreaktionen in Lösungen." Naturwissenschaften, 23, 64 (1935).
7. Holluta, J., and Eberhardt, M., "Über geschlossene Enteisung durch Schnellfiltration." Vom Wasser, XXIV p. 79, Weinheim/Bergstr, Verlag Chemie GMBH (1957).
8. Feitknecht, W., "Über die Oxydation von festen Hydroxverbindungen des Eisens in wässrigen Lösungen." Z. Elektrochem., 63, 34 (1959).
9. Hauer, G. E., "Iron and CO<sub>2</sub> Removal." Jour. A.W.W.A., 42, 6, 555 (1950).
10. Bouthillier, P. H., "Removal of Iron from Water." Municipal Utilities, 89, 1, 28 (1951).
11. Mathews, E. R., "Iron and Manganese Removal by Free Residual Chlorination." Jour. A.W.W.A., 39, 7, 680 (1947).
12. Ley, C., "A Unique Iron Removal Plant." Jour. A.W.W.A., 30, 9, 1943 (1958).
13. Humphrey, S. B., and Eikleberry, M. A., "Iron and Manganese Removal Using KMnO<sub>4</sub>." Water and Sewage Works, Ref. No. R-176 (1962).
14. Applebaum, S. B., and Bretchen, M. E., "Removal of Iron and Manganese from Water." Jour. A.W.W.A., 3, 6, 400 (1916).
15. Babcock, R. H., "Iron and Manganese in Water Supplies and Methods of Removal." Water and Sewage Works, 98, 10, 442 (1951).
16. Fosnot, H. R., "Seven Methods of Iron Removal." Pub. Wks., 86, 11, 81 (1955).



17. Longley, J. M., "The Removal of Iron from Water by Aeration and Filtration." M.S. Thesis, Univ. of Illinois (1961).
18. Van der Wal, S. S., "Removal of Iron from Ground Water by Adsorption." *Water (Neth.)*, 36, 1 (1952). Abs. Jour. A.W.W.A., 44, 10, 42 P and R (1952).
19. Babcock, R. H., "Iron and Manganese Removal by Spaulding Precipitator." Jour. N.E.W.W.A., 64, 2, 138 (1950).
20. Weston, R. S., "The Purification of Ground Water Containing Iron and Manganese." Trans. ASCE, 64, 112 (1909).
21. Leclerc, E., and Beaujean, P., "Research Relating to Iron Complexes." Bull. Mens. Centre Belge Etude Document Eaux, 56, 170 (1955). Abs. WPA, 1069 (1958).
22. Beneden, G. V., Bull. Centre Belge Etude et Document (Liege), 43, 49 (1959). Abs. Jour. A.W.W.A., 52, 7, 64 P and R (1960).
23. Boorsma, H. J., "Les Principes de la Deferrisation, de la Demanganisation et de la Nitrification dans la Pratique de L'epuration des Eaux Souterraines." XXVII<sup>e</sup> Congrès de Chimie Industrielle à Bruxelles, I, 340 (1954).
24. Komolrit, K., "Measurement of Redox Potential and Determination of Ferrous Iron in Ground Waters," M.S. Thesis, Univ. of Illinois (1962).
25. Robinson, L. R., Jr., "The Presence of Organic Matter and Its Effect on Iron Removal in Ground Water." Ph.D. Thesis, Univ. of Illinois (1963).
26. Stumm, W., and Lee, G. F., "The Chemistry of Aqueous Iron," Schw. Zeit. Hydrologie, 32:295 (1960).
27. Morgan, J. J., and Stumm, W., "The Role of Multivalent Metal Oxides in Limnological Transformations, as Exemplified by Iron and Manganese." Paper No. 6, Presented at the Second International Conference on Water Pollution Research, August (1964).
28. Hem, J. D., and Cropper, W. H., Survey of Ferrous-Ferric Chemical Equilibria and Redox Potentials, U.S. Geol. Survey Water Supply Paper No. 1459-A (1960).
29. Hem, J. D., Restraints on Dissolved Ferrous Iron Imposed by Bicarbonate, Redox Potential, and pH. U.S. Geol. Survey Water Supply Paper No. 1459-B (1960).
30. Stumm, W., and Lee, G. F., "Oxygenation of Ferrous Iron." Ind. Eng. Chem., 53:143 (1961).
31. Stumm, W., "Chemistry of Natural Waters in Relation to Water Quality." Symposium Environmental Measurements, U.S.P.H.S. Pub. No. 999-WP-15:299 (1964).



32. Leussing, O. L., and Kolthoff, J. M., "The Solubility Product of Ferrous Hydroxide and the Ionization of Aquo-Ferrous Ion." Jour. Amer. Chem. Soc., 75:2476 (1953).
33. Latimer, W. M., Oxidation Potentials, 2nd ed., Prentice Hall, Inc., New York (1952).
34. Fair, G. M., and Geyer, J. C., Water and Waste-Water Disposal, John Wiley & Sons, Inc., New York (1963).
35. Gayer, K. H., and Woontner, L., "The Solubility of Ferrous Hydroxide and Ferric Hydroxide in Acidic and Basic Media at 25°C." Jour. Phys. Chem., 60:1569 (1956).
36. Just, G., "Kinetische Untersuchung der Autoxydation des in Wasser gelösten Ferrobicarbonates." Ber. deut. Chem. Gesell. (Berlin), 40, 3695 (1907).
37. Just, G., "Kinetische Untersuchung der Autoxydation des Ferrobicarbonates." Z. phys. Chem., 63, 385 (1908).
38. Abel, E., "Über Autoxydation in umbelichteter homogener wässriger Lösung. Mit besonderer Berücksichtigung anorganischer Systeme." Z. Elektrochemie, 59, 903 (1955).
39. Cher, M., and Davidson, N., "The Kinetics of Oxygenation of Ferrous Iron in Phosphoric Acid Solutions." Jour. Amer. Chem. Soc., 77, 793 (1935).
40. Pourbaix, M. J. N., Thermodynamics of Dilute Aqueous Solutions, E. Arnold Publishing Co., London (1949).
41. Delahay, P., Pourbaix, M., and Rysselberghe, P. V., "Potential-pH Diagrams." Jour. Chem. Educ., 27, 12, 683 (1950).
42. Goswami, S. R., "The Relation of the ORP to the Ferrous-Ferric Equilibrium in Ground Waters." M.S. Thesis, Univ. of Illinois (1965).
43. Larson, T. E., "Oxidation of Metals and Ions in Solution." Paper presented at the Fourth Rudolfs Research Conference, Rutgers University, New Brunswick, New Jersey (June, 1965).
44. O'Connor, J. T., Ghosh, M. M., and Engelbrecht, R. S., "Rate of Precipitation of Iron in Aerated Ground Waters." Paper presented at the ASCE National Sanitary Engineering Symposium, University Park, Pa. (July, 1965).
45. Heertjes, P. M., and Lerk, C. F., "Some Aspects of the Removal of Iron from Groundwater." Proc. Symposium on the Interaction between Fluids and Particles, London, p. 270 (June, 1962).
46. Hutchinson, G. E., A Treatise on Limnology, Vol. I, John Wiley & Sons, New York (1957).



47. Bjerrum, J., Schwarzenbach, G., and Sillén, L. G., "Stability Constants of Metal Ion Complexes." Special Publication No. 6 and 7, The Chem. Soc., London (1958).
48. Robinson, L. R., Jr., Personal Communications.
49. Thomas, A. W., and Whitehead, T. H., "Ion Interchanges in Aluminum Oxychloride Hydrosols." Jour. Phys. Chem., 35, 27 (1931).
50. Thomas, A. W., and Tai, A. P., "The Nature of Aluminum Oxide Hydrosols." Jour. Amer. Chem. Soc., 54, 841 (1932).
51. Stumm, W., and Morgan, J. J., "Chemical Aspects of Coagulation." Jour. A.W.W.A., 54, 8, 972 (1962).
52. Riddick, T. M., "Zeta Potential and its Application to Difficult Waters." Jour. A.W.W.A., 53, 8, 1007 (1961).
53. Riddick, T. M., "Zeta Potential: New Tool for Water Treatment, Part I." Chem. Engr., 68, 13, 121 (1961).
54. Riddick, T. M., "Zeta Potential: New Tool for Water Treatment, Part II." Chem. Engr., 68, 14, 141 (1961).
55. Baylis, J. R., "Discussion of Rapid Sand Filtration." Jour. A.W.W.A., 15, 673 (1926).
56. Baylis, J. R., "Experiences in Filtration." Jour. A.W.W.A., 29, 1010 (1937).
57. Stanley, D. R., "Sand Filtration Studies with Radio Tracers." Proc. ASCE, 81, Sep. No. 592 (1955).
58. Hall, W. A., "An Analysis of Sand Filtration." Proc. ASCE, 83, Sep. No. 1276 (1957).
59. Stein, P. C., "A Study of the Theory of Rapid Sand Filtration of Water through Sand," Mass. Inst. of Tech., Ph.D. Thesis (1940).
60. Tso-Ti Ling, J., "A Study of Filtration through Uniform Sand Filters." Proc. ASCE, 81, Paper No. 751 (1955).
61. Baylis, J. R., "Chicago South District Filtration Plant." Jour. A.W.W.A., 41, 7, 599 (1949).
62. Geyer, J. C., and Machis, A., "Final Report on Investigations, Water Filtration Research, 1947-1949." Contract No. W44-009, eng-460, Eng. Res. Div. Lab., Fort Belvoir, Virginia (Aug., 1949).
63. Iwasaki, T., "Some Notes on Sand Filtration." Jour. A.W.W.A., 29, 1591 (1937).
64. Ives, K. J., "Rational Design of Filters," Inst. Civ. Engineers (British), Paper No. 6414 (1960).



65. Cleasby, J. L., and Baumann, E. R., "Selection of Optimum Filtration Rates for Sand Filters." Bull. No. 198, Iowa Eng. Expt. Stn., Univ. of Iowa, Ames, Iowa (1962).
66. Winogradski, S., "Über Eisenbakterien." Botanische Zeitung, 46, 261 (1888). Bot. Z., 46, 261 (1888).
67. Thimann, K. V., Life of Bacteria, McMillan Co., New York (1963).
68. Hutchinson, G. E., Treatise on Limnology, John Wiley & Sons, New York (1959).
69. Oborn, E. T., and Hem, J. D., "Some Effects of the Larger Aquatic Vegetation on Iron Content of Water." U.S. Geol. Survey Water Supply Paper No. 1459-I (1962).
70. Cholodny, N., "Zur Morphologie der Eisenbakterien, Gallionella und Spirophyllum." Ber. Botan. Ges., 42, 35 (1924).
71. Pringsheim, E. G., "Iron Bacteria." Biol. Revs., Cambridge Phil. Soc., 24, 200 (1949).
72. Lieske, R., "Beiträge zur Kenntnis der Physiologie von Spirophyllum ferrugineum Ellis einem typischen Eisenbakterium." Jahrb. Wiss. Bot., 49, 91 (1911).
73. Starkey, R. L., "Precipitation of Ferric Hydrate by Iron Bacteria." Science, 102, 532 (1945).
74. Dorff, P., "Die Eisenorganismen. Systematik und Morphologie." Pflanzenforschung. Ed. R. Kolkwitz. Jena, G. Fischer (1934).
75. Wolfe, R. S., "Cultivation, Morphology, and Classification of the Iron Bacteria." Jour. A.W.W.A., 50, 9, 1241 (1958).
76. Leatham, W. W., Kinsell, N. A., and Braley, S. A., Jr., "Ferrobacillus Ferrooxidans: A Chemosynthetic Autotrophic Bacterium." Jour. Bact., 72, 700 (1956).
77. Silverman, M. P., Lundgren, D. G., "Studies on the Chemoautotrophic Iron Bacterium Ferrobacillus Ferrooxidans." Jour. Bact., 77, 642 (1959).
78. Colmer, A. R., Temple, K. L., and Hinkle, M. E., "An Iron-Oxidizing Bacterium from the Acid Drainage of Some Bituminous Coal Mines." Jour. Bact., 59, 317 (1950).
79. Clark, F. W., Personal communication, Dept. of Microb., Univ. of Ill., Urbana, Ill.
80. Meyerhof, O., Pflüger's Arch. ges. Physiol., 166, 245 (1917).
81. Lees, H., and Quastel, J. H., "Biochemistry of Nitrification in Soil." Biochem. Jour., 40, 803 (1946).
82. Quastel, J. H., and Scholefield, P. G., "Biochemistry of Nitrification in Soil." Bact. Revs., 15, 3, 1 (1951).



83. Hofman, T., and Lees, H., "The Biochemistry of the Nitrifying Organisms." Biochem. Jour., 54, 4, 579 (1953).
84. Lees, H., "The Biochemistry of Nitrifying Organisms. I. The Ammonia-Oxidizing Systems of Nitrosomonas." Biochem. Jour., 52, 134 (1952).
85. Buswell, A. M., "Microscopic Growths in Distribution Systems and Their Food Supply." Jour. A.W.W.A., 30, 10, 1651 (1938).
86. Kooijmans, L. H. L., International Water Supply Congress & Exhibition, Subject No. 4, Aeration and Deferrization, Intl. Water Supply Assocn., London (July, 1955).
87. Feben, D., "Nitrifying Bacteria in Water Supplies." Jour. A.W.W.A., 27, 4, 439 (1935).
88. Larson, T. E., "Bacteria, Corrosion and Red Water." Jour. A.W.W.A., 31, 7, 1186 (1939).
89. Hill, J. C., "Bacterial Oxidation of Ammonia in Circulating Water." Jour. A.W.W.A., 38, 8, 980 (1946).
90. Boorsma, H. J., and Peelan, R., "Iron, Ammonia and Manganese Removal by Auto-Oxidation in Non-Submerged Filters." General Papers, Symposium on Chemistry of Water Supplies, Amer. Chem. Soc., Div. of Water and Waste Chemistry (March, 1962).
91. Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 11th Edition, American Public Health Association, Inc. (1960).
92. Lee, G. F., and Stumm, W., "Determination of Ferrous Iron in the Presence of Ferric Iron with Bathophenanthroline." Jour. A.W.W.A., 52, 12, 1567 (1960).
93. Ghosh, M. M., "The Evaluation of Bathophenanthroline Method in the Determination of Soluble and Total Ferrous Iron in the Presence of Ferric Iron in Natural Waters." (Unpublished)
94. Painter, H. A., and Jones, K., "The Use of the Wide-Bore Dropping-Mercury Electrode for the Determination of Rates of Oxygen Uptake and the Oxidation of Ammonia by Microorganisms, J. Appl. Bact., 26, 3, 471 (1963).
95. Eliassen, R., "Clogging of Rapid Sand Filters." Jour. A.W.W.A., 33, 926 (1941).
96. Ghosh, M. M., "Pilot Plant Studies on Iron Removal." Paper presented at the 56th Illinois Section Meeting of the A.W.W.A. (March, 1965).
97. Engelbrecht, R. S., O'Connor, J. T., and Ghosh, M. M., "Significance and Removal of Iron in Water Supplies." Paper presented at the Fourth Annual Sanitary and Water Resources Engineering Conference, Vanderbilt University, Nashville, Tennessee (June, 1965).
98. Camp, T. R., Water and Its Impurities, p. 222, Reinhold Publishing Corporation, New York (1963).



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  3. O'Connor, J. T., Ghosh, M. M., and Engelbrecht, R. S., "The Rate of Precipitation of Iron in Aerated Ground Waters." Presented at the National Symposium on Sanitary Engineering Research, Development and Design, University Park, Pa., July, 1965.





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